THE IGNITION OF COMBUSTIBLE GASEOUS MIXTURES BY HOT PARTICLES

(with an Appendix on a correlated problem in the Conduction of Heat between a Solid and a Gas)

by

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Thesis

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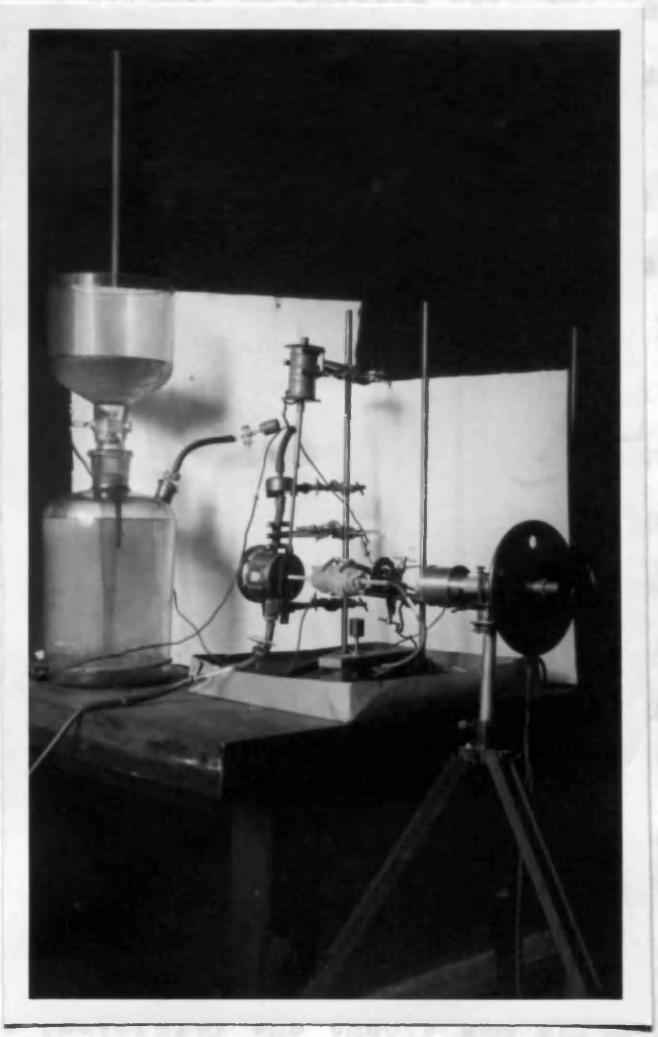

General View of Hot Particle Ignition Apparatus.

PREFACE.

I have been allowed to present this thesis to Glasgow University by the kind decision of the senate to consider as a third year within the meaning of the regulations, the year which I spent on the research staff of Imperial Chemical Industries (Explosives) at Ardeer, subsequent to my two years (1934-1936) as a matriculated research student in the Natural Philosophy department. For this decision I am grateful. All the experimental work recounted in the thesis was done during the time in the Natural Philosophy department, as holder of the Thomson Research Scholarship and the Houldsworth Research Studentship which supplemented the research grant which I then held from I.C.I. I should like to acknowledge my indebtedness to the University and to I.C.I. for the assistance thus provided.

The matter in the appendix on a specific heat conduction problem was also developed during the matriculated period, and a beginning was then made with the theory of the ignition process. After leaving the University the theory was further developed and applied to the experimental results until it was possible to present it in the fairly complete form given in the thesis. Subsequent experience at Ardeer led also to a further examination of the possibility of the occurrence of chain explosions, and to the development of the practical illustrations which have been given.

The apparatus was designed by myself and made in the department workshop. The experiments were carried out without assistance and, so far as I am aware, the theory is an original development obtained by applying generally accepted fundamental principles of ignition to the particular case under consideration. I have attempted to give full references in the text whenever a statement is made which is neither an argument of my own nor a repetition of some well-known general principle.

For a neater text, I have thought it advisable to use for certain of the figures cuttings from reprints of papers which I published in the "Philosophical Magazine"* and which dealt with some portions of the work recounted in the thesis.

I wish to acknowledge the helpful encouragement which I received from Professor E. Taylor-Jones while under his supervision and for his continued interest in the progress of the work since I left.

Dr J. Weir and Dr A. G. White of the Research staff at Ardeer also showed encouraging interest in the work throughout.

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* September 1936. Vol. 22, p. 466. and April 1937 Supplement. Vol. 23, p. 633.

C O N T E N T S

B. APPENDIX.

On the application of certain Heat Conduction Solutions for a uniform medium to the Temperature distribution in the gas surrounding a metal sphere.

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1. INTRODUCTION.

The subject matter of this thesis is, so far as the writer is aware, the first attempt to investigate the power of a single hot particle to ignite combustible gaseous mixtures. It is related to practical questions of considerable importance, notably the explosion of methane-air mixtures in coal-mines, and was suggested as of interest for research by Dr A. G. White of Imperial Chemical Industries (Explosives) Research Section at Ardeer.

The potential sources of hot particles in coal-mining are many and varied in their nature. Falls of roof, collapse of supports, dropping out of stones from the roof, can all give rise to frictional effects, and such occurrences have been reported to be succeeded by explosions of firedamp. It has been thought that small rock pieces heated by the friction may cause ignition. Other possible causes, however, arise in these occurrences such as sudden compression of pockets of the gas which may heat adiabatically, and outbursts of flame from broken lamps. Moreover, considering the rapid sequence of such events and their effects on surviving observers it may clearly be somewhat uncertain as to which is the initial event. However, in the operations involved in bringing down sections of the coal face by blasting, definite possibility of the presence of hot particles arises in different ways. In general practice the coal about to be blasted is first undercut, at the floor, and frictional sparks can easily occur

from the working of picks or machine cutters in the process. The same can be said of the drilling of the borehole into which the explosive charge is inserted. Black powder fuse, which gives a train of sparks, is not now used in fiery mines, the detonator being initiated electrically. The detonation of the detonator and of the explosive charge is, however, a very likely source of hot particles, and it is this source which is of the greatest interest.

From the nature of the phenomena accompanying the detonation of a cartridge of explosive, it is however to be expected that more potent causes of ignition of the surrounding gas medium occur, namely the flame from the explosive, the high temperature gaseous products, and the compression wave engendered. These are so predominant that until recently the possibility of ignition by hot solid particles from the detonation was omitted from consideration. This is evident when we search through the regulations governing the use of explosives in fiery mines. As a result of experience, empirical rules have been drawn up, but in most countries these deal exclusively with the nature and size of charge the method of initiation and the method of loading the borehole. In France an attempt was made to give official regulations having a basis in theory. According to the regulations of 1890, only explosives of calculated combustion temperature less than 1500°C, with sufficient oxygen in their composition for the complete combustion of all carbon and hydrogen, were permitted. The belief at the back of this was that products of explosion would be hot

enough to ignite fire-damp if their temperature was greater than 1500°C, and that, with insufficient oxygen, carbon monoxide and hydrogen ejected from the shot and inflaming subsequently in the atmosphere, were causes of igniting the firedamp.

The fundamental aims of such regulations are

(a) to control the size of flame emitted by the methods of initiation and loading;

(b) to control the pressure wave;

(c) to control the temperature of explosion gases by suitable explosive substances.

The flame and the pressure wave were thus the only suspected causes of ignitions of the surrounding explosive atmosphere. However, at the International Conference on Safety in Mines, held at Buxton in 1931, a paper was given by Dr E. Beyling[2], in which he described experiments which seemed to show that neither the flame nor the pressure could always be responsible for ignition. Beyling concluded that the probable cause when neither of these could be suspect, was hot particles of undecomposed explosive, or hot particles of cartridge casing, stemming etc. In the discussion after Beyling's paper, M. Audibert remarked that he believed that the first group, i.e. particles of undecomposed explosive, were a very likely cause.

At this stage the problem may be linked up with the history of attempts to investigate the ignition of firedamp by frictional sparks. The general results of such investigations are summarised by Coward and Wheeler in their section on Frictional

Sparks[1]. The total of the evidence is inconclusive. Recent investigations have been performed by M. J. Burgess and R. V. Wheeler[3]. The general trend of their results is that frictional sparks will hardly produce ignition of methane. In the cases where they did obtain ignitions, they draw attention to the heat developed in the contacting surfaces. Again their experiments on coal-cutter picks seemed to indicate that when ignition occurred it was due to a heated area of rock produced by the cutters, rather than to the sparks given by the rock.

Now considering frictional sparks as small hot particles which are not undergoing combustion, the negative results of the attempts are important to the present subject. But from first principles it is very probable that the size and temperature of a particle will be prominent factors in determining its ability to cause ignition. It is hoped that the work recounted in this thesis will serve as a beginning towards the investigation of the importance of these factors and of the relationships existing between them.

At this point we may profitably consider the difference between hot undecomposed particles of explosive and hot pieces of inert matter as regards general factors which would effect gas ignition. Particles of hot inert matter such as metallic fragments, if they ignite at all must do so solely by virtue of their initial temperature. An undecomposed particle of explosive at a high temperature will, however, be reacting, hot carbonaceous matter will burn. Additional factors are therefore brought into

play, namely the production of more heat, by the reaction or oxidation, and the formation of reaction products, normally gaseous consisting mainly of oxides of carbon and water. The importance of these will be discussed in Part II in the light of the literature which is reviewed in the following section.

2. LITERATURE.

Apart from methane, the present investigations dealt largely with ignitions of coal-gas-air, hydrogen-air, and pentane-air, mixtures, and mention will now be made of the known properties of some such mixtures. The possible variations in composition of a coal-gas supply make experiments with it of little quantitative value, and little mention of ignition temperatures of coal-gas-air mixtures appears in the literature.

Methane, hydrogen, and pentane have, however, been extensively investigated from many standpoints. The figures in Table I have been taken from Bone and Townend[4], and show the average ranges of inflammability of the three gases when mixed with air.

TABLE I.

IGNITION RANGES.

Gas	Percentages in inflammable mixtures with air
Methane	5 - 13
Pentane	1.5 - 5
Hydrogen	9 - 65

Outside these limits flame will not propagate through the mixture. Within the limits the mixtures may be exploded by suitable igniting means, such as an electric spark or a flame. Much work has also been done on the determination of ignition temperatures, which are taken to be the temperature to which an inflammable mixture is raised under given conditions before exploding. The measurement of such temperatures gives valuable evidence on the comparative inflammability of different gas mixtures. An important feature which has been shewn to occur if the time lag which elapses between the mixture reaching the temperature and its explosion. H. B. Dixon has investigated this effect very thoroughly, and his work is fully reviewed by Bone and Townend[5]. He found that, for all the gases with which he worked there were time lags of ignition at certain temperatures and his results for methane and hydrogen are given in Table II.

TABLE II.

INFLUENCE OF LAG ON IGNITION TEMPERATURE. (Dixon)

Methane	Ign. Temp.	746	728	710	674	657	
	Lag (Secs.)	0.6	1.0	2.0	3.0	10.0	
Hydrogen	Ign. Temp.	630	619	605	588	577	572
	Lag (Secs.)	0.5	1.0	2.0	5.0	10.0	15

We see that for the same lag, the ignition temperature of hydrogen is considerably less than that of methane. Methane, indeed, shews a very high ignition temperature compared with the other gases of the paraffin series.

In Dixon's experiments, the combustible gas and air flow separately to mix in the heated chamber. His results, therefore, give no indication of the effect of composition of the mixture. The effect was investigated by Mason and Wheeler[6], for the paraffin gases. Table III shews their results for methane and pentane.

TABLE III.

IGNITION TEMPERATURES OF VARIOUS COMPOSITIONS.

Methane Percentage	Ignition Temperature	Pentane Percentage	Ignition Temperature
2.45	690	1.5	548
4.05	684	2.15	532
6.0	685	2.75	520
8.0	692	3.75	502
10.15	703	5.30	486
11.4	711	7.65	471
12.8	720		

Mason and Wheeler state that the general value for the lag with methane was 10-16 seconds at these temperatures, but decreased rapidly as the methane content increased beyond 9.45%, a 12.8% mixture giving 6.6 seconds at 720°. For pentane a lag of about fifteen seconds occurred with percentages 1.5 to 3.95, and for a 7.65% mixture 5 seconds. Pentane is therefore much more readily ignited than methane and indeed judging by this criterion Mason and Wheeler found it relatively the most readily ignited in the series from methane to pentane.

Stress is being laid on the literature dealing with the relation between time lag and ignition temperature because it may easily be seen to be of considerable importance in the ignition of gases by hot particles. Experiments such as those described above involve the admission of the gas mixture to an enclosure maintained at the required temperature. A small hot body travelling through an otherwise cold gas mixture is not however in contact with any portion of the gas for any appreciable time. If it is to cause ignition it is then clear that its temperature must at least be such as to indicate a very small time lag. The possibilities inherent in this may be seen from Naylor and Wheeler's work on methane. For a 6.5% mixture in air they found a lag of nearly 11 seconds at 100°C, while 1175°C was required to reduce the lag to $^{1}/_{100}$th of a second. Temperatures required in moving hot particles may therefore be considerably greater than the commonly accepted ignition temperatures.

Now ignition by heated metal bars and by hot wires approaches to the particle case in that, because of convection currents, the gas does not remain for more than a brief period of time at the temperature attained by contact with the metal. Again, then, one would expect the lowest temperature at which a metal bar would inflame methane-air mixtures to be one for which the time lag was short. Some results on metal bars are given by Coward and Wheeler(7). No mixture of methane was ignited by a nickel bar until the bar was above 1025°C. A straight line is shown when igniting temperature of the nickel bar is plotted against percentage of methane, the temperature rising for increasing concentration. The experiment was performed for various metals and steels, which give graphs similar to that of nickel. The curve for platinum was abnormal in that it rose to a peak at over 1400°C for 9 per cent. and then fell away, but at all its points it was much higher than the others. Coward and Wheeler, on the basis of work done by Coward and Guest(8), suggest that this is probably due to the high catalytic activity of platinum. The conclusion from the experiments is that no bar of heated material is capable of igniting methane unless its temperature is at least near 1000°C, almost white heat.

While ignition by heated wires might be taken as a further approach to the particle case, the work of Shepherd and Wheeler(9) shows that the problem is complicated by the current fusing the wire. No sufficiently confirmed relevant matter appears in this type of ignition.

Lastly, reference may be made to work of J. W. Mc David in the Nobel Research Laboratories at Ardeer[10]. He aimed at eliminating the lag as far as possible, the express object of his experiments being to determine the minimum temperature to which a given gaseous mixture must be heated, by the sudden application of a heated body, so as to cause its instantaneous ignition. The heated body was a small electrically heated wire - he compared results with Eureka alloy and platinum coils wound on a small silica tube in which was a thermo-junction to measure the temperature. This was applied to a bubble of the gas formed in glycerine. He concluded definitely that "pure methane when mixed with air does not ignite below 1000°C.," i.e., for the short time-lag given by this method. For a coal-gas air mixture he found an ignition temperature of 818°C., and states that, within the limits of explosive mixtures, the variation of percentage of air in the mixture does not cause great variation in the temperature observed for ignition. As regards his aim of obtaining an instantaneous ignition, it seems probable that the method of the present work will give a closer approximation, for in this case the hot body is a particle in rapid motion through the gas mixture, whereas his heated wire was merely placed against the bubble.

PART II. EXPERIMENTAL PROCEDURE AND RESULTS.

PART II.

Section 1.

Introduction - The Effect of Reaction in the Particle.

The attack on the problem was adopted with reference to the literature reviewed in Part I. It was decided, in the first place, to use metallic particles which would not undergo combustion. The differences between such a particle and a piece of reacting or combustible substance have been given in our introduction, and from the information summarised in the preceding section we can now estimate their importance.

The primary effect in the burning particle is the production of heat, which affords a compensation for radiation and conduction losses which is entirely absent in the case of the non-burning body. The temperature of the former may therefore be raised even above its initial temperature, and certainly under similar conditions of size, initial temperature, specific heat etc., it will maintain its temperature longer than the latter. For this reason, therefore, it must offer a greater potentiality of ignition, since it can more readily fulfil time lag requirements. A secondary effect is the presence of gaseous reaction products such as carbon dioxide and water. In some cases carbon monoxide may also be formed and may itself ignite, the consequent flame readily igniting the surrounding mixture, (cf. French regulations, discussed on p. 6). A less obvious, but equally important result of reaction or combustion is the fact that the carbon dioxide and water must mix with the surrounding gas mixture, and in general diminish the percentage of combustible

gas present in a given volume. This is important since it is clear that by doing so, a very rich mixture which is not ignitable may be brought to a concentration within the ignition range, while at the other end a lower limit mixture may be rendered too poor in combustible gas concentration for ignition. It would seem, therefore, so far as the effect is concerned, that for rich igniting mixtures a burning particle would ignite more readily than a non-burning particle, ceteris paribus. For mixtures poor in combustible gas the opposite would be the case. Further, from many explosives, oxides of nitrogen are produced, and these, as well as water vapour can have a catalytic influence on gaseous reactions.[11] Summing up these factors we may say then that it is highly probable that if a non-burning particle can ignite a gas mixture, the other effects which occur with a similar particle capable of reaction or combustion will intensify its power of ignition.

For this reason, the experimental work described in this thesis was confined to the investigation of the fundamental phenomenon of direct thermal ignition. Platinum was decided upon as a first substance capable of exposure to high temperatures with only very slight oxidation, and later, quartz which has a similar property, was used for comparison with platinum.

Section 2.

Preliminary Experiments.

We first proceeded to try qualitatively the possibility of particle ignitions. The information gleaned from these experiments proved useful in determining the final apparatus.

Red-hot steel ball-bearings introduced in the coal-gas air mixture stream from a bunsen burner failed to cause ignition. So also did iron filings heated to redness in a crucible and then poured over the jet . These experiments demonstrated the need for heating apparatus capable of giving temperatures well over 700°C. Actual ignitions of coal-gas air mixtures by hot particles were obtained in a very simple manner. A brass cap with a small hinged opening was fitted over a closed glass tube, and a toy firework "squib" held in a retort stand so that when lit it directed a stream of sparks against the cap. Explosions of a coal-gas air mixture at atmosphere pressure in the glass tube were obtained then by opening the hinged aperture and allowing sparks from the squib to enter. It was found that a diaphragm of commercial "Cellophane" over the other end of the glass tube gave air-tight closure, while shattering easily when ignition occurred so that the pressure generated was released and the glass tube remained undamaged. This principle was used in the final apparatus.

The possibility of particle ignitions of coal-gas air mixtures thus established, we proceeded to the planning of apparatus suitable for quantitative investigation.

Section 3.

Final apparatus.

It was decided to use spherical particles as being the simplest regular form. The construction of suitable apparatus and the development of suitable experimental technique presented many difficulties, some of which are of interest - as an example we may mention one form of apparatus which was tried. In it the principle was to drop the particle vertically into an explosion chamber, the particle being electrically heated by a resistance woundround a tube. It was eventually abandoned for the following reasons:-

(a) Difficulty in temperature measurement. The sphere had to be loose in order to fall, and so a thermocouple could not be connected to it.

(b) The convection up the tube caused very inefficient heating of the particle.

(c) The greatest difficulty was to devise a trap door, platform, and a diaphragm arrangement to allow the sphere to fall and to open the explosion chamber at the correct time. Any platform used has to remain mechanically efficient while at the same temperature as the particle.

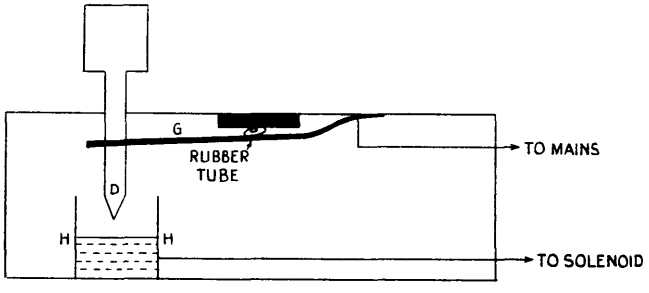
In the apparatus eventually adopted the particle was heated in a horizontal tube. Thus the first of the above difficulties was overcome by using an optical pyrometer, while the second ceased to exist. After several trials an arrangement was

devised which would admit the particle to the gas mixture. The main features of the apparatus are apparent from fig. 1 which represents a vertical section.

The explosion chamber on the left was formed from a brass cylinder, of diameter 8.2 cm. At one end this was closed by a brass plate in which a hole 6 mm. in diameter was made. To the other end a brass ring was soldered, R in fig. 1, forming a rim for the tube. A sheet of commercial cellophane was held between two rubber rings placed on the rim, and a brass cover-ring C of the same dimensions as the rim screwed down, thus effectively closing this end. Outside the hole in the other end a slide S was constructed. In the slide was a Slit Sl 6 mm. broad and 2.3 cm. long. This, sliding past the hole, served to open the chamber to admit the sphere. The gas inlet and outlet, each of which had a stop-cock, were on opposite sides of the cylindrical wall of the chamber, in which was also a small window. A brass strip was soldered into the chamber to form a target T which the sphere would strike, in order to prevent it shooting through the cellophane. The slide was attached to the soft iron rod L slipped into the hollow core of a solenoid.

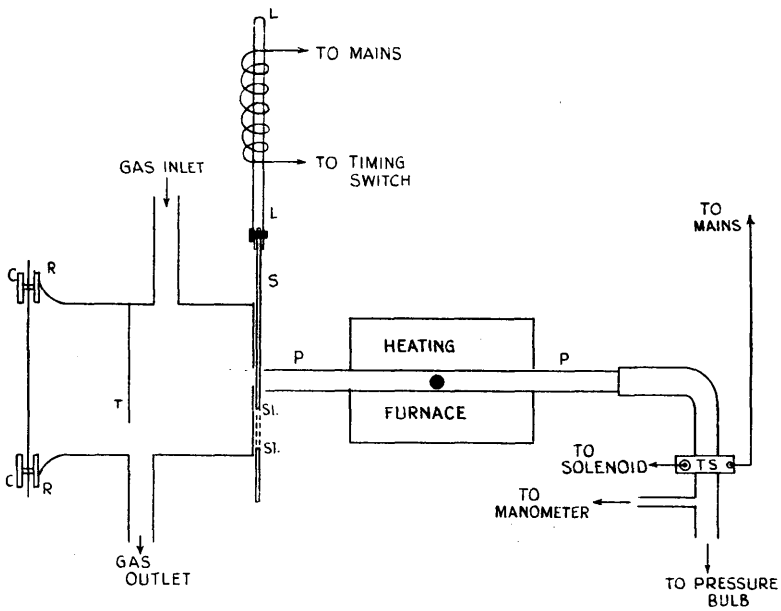
The particle was heated by a coil of either nickel chrome alloy or platinum wire wound round a silica or porcelain tube P, which was set in alignment with the hole in the chamber. The shooting apparatus consisted of a hand-pressure bulb B connected through the timing switch TS to the end of the heating tube and to a manometer. The timing switch is shown in detail in fig. 2

Fig. 2.



See next page for figure 1. The figure was misplaced in binding.
R.S.S.

Fig. 7.


L
TO MAINS
TO TIMING SWITCH
GAS INLET
L
S
C
R
T
P
HEATING
FURNACE
P
Sl.
Sl.
C
R
TO MAINS
TO SOLENOID
TS
TO MANOMETER
GAS OUTLET
TO PRESSURE BULB

The brass strip G there acts as a spring which constricts the rubber tubing leading from the pressure bulb to the heating tube. In fig. 2 this constriction is shown in section. The cup H contains mercury into which the dipper D may be pushed, closing the solenoid circuit. This also releases the pressure by depressing G so that the particle is shot along while the slide travels up. Adjustment for correct timing may be made by altering the mercury level or by the amount of friction between the iron rod and the solenoid core, and so the particle may be made to arrive at the end of the tube just as the hole is open. The winding on the tube P was covered first by a layer of fire-clay, and then by a winding of asbestos string.

The method of taking observations consisted in the following procedure. The gas mixture was made up over water in a gasholder and allowed to stand to ensure a thoroughly diffused mixture, and the rubber tube from the gasholder was connected to the gas inlet. The sphere was placed in the quartz tube and the heating current switched on, at a value which would give a higher temperature than the one being investigated. A previously standardized optical pyrometer was set to measure the temperature by looking along the heating tube from the end distant from the explosion chamber, the leading tube from the pressure bulb being at this stage not affixed to the end. When the temperature of the ball had become higher than was required, the current was cut down, and the rheostats in the heating circuit adjusted until the temperature reached and remained steady at the required

value. This done, the leading tube from the pressure bulb and timing switch was connected to the end of the heating tube, ready to blow out the particle. The gas mixture was then turned on to run through the explosion chamber, the outlet leading to a burner set with its mouth to a flame, so as to burn up the issuing gas. The mixture was allowed to run through for a time sufficient to expel the original air and ensure the required concentration in the chamber. This could be judged by the appearance of the jet issuing at the burner. The gas outlet and inlet were closed, the former first, to avoid the risk of air re-entering. This left the mixture in the chamber with a pressure slightly greater than atmospheric, causing a bulge in the cellophane cover. The outlet stop-cock was then rapidly opened and shut, to release this pressure, and then the release key depressed. If the particle did not enter, the timing arrangement was adjusted and the experiment repeated. When it went in, if an ignition occurred, the cellophane sheet was shattered by the explosion. In the adjustment of the pressure bulb it was always set to the same pressure, measured on an open manometer, for any one particle, so that an approximately constant velocity of firing might be obtained. The effect of varying velocity has not been investigated in the present work, although in view of the time-lag discussed in ~~Section~~ Part 1 it may be of importance. The speeds used were measured by a trajectory method and were of the order of 4 metres per second, but may vary between 2 and 5 metres per second.

The general appearance of the apparatus is shown in Plate 1, where the objective of the optical pyrometer is seen to the right pointing to the quartz tube. As a matter of interest, it may be stated that the photograph was taken with an ordinary Kodak snapshot camera and film, exposure 14 sec., at f.16.

Note on Measurement of Temperature.

The scale-readings on the pyrometer are correctly calibrated only for black-body conditions. As shown in fig. the heating coil was surrounded with clay and asbestos wrapping. Since the coils were usually from 5 to 6 cm. in axial length, there was a fairly uniformly heated portion of tube on each side of the sphere. Moreover, the particle was always at least 10 cm. from the end of the tube. The radiation entering the pyrometer is thus contained in a very small solid angle. For this reason and since radiation from the ball is reflected from the walls of the tube, the conditions under which the temperature is being measured approach black-body conditions. This is important, since for platinum Waidner and Burgess[19] have shown that a correction, varying from 70° at an apparent temperature of 800° to over 200° at an apparent temperature of 1500°, has to be added to the apparent temperature as read by the pyrometer if it is only direct radiation from the platinum that is being observed. The conditions in our case, while not exactly black-body conditions, are much closer approximations to them than to those of direct observation. The temperatures given in the tables of results are thus the direct scale readings of the pyrometer.

Section 4.

Results.

(a) Methane-air mixtures. First attempts were made with the above apparatus using methane-air mixtures of concentration 10% methane. Spheres of platinum from 1 mm. to 4 mm. in diameter were tried, but no ignitions were obtained up to the highest temperature attainable with the heating coils in use, namely about 1300°C. Above this temperature the heating coils failed too rapidly to allow of experiments being made.

(b) Coal-gas air mixtures. In the preliminary experiments, ignitions of coal-gas with air had been obtained. Accordingly, when faced with the negative results of the attempts with methane, we decided to investigate the particle problem in the first place with coal-gas air mixtures. By this means it was hoped that at least general qualitative characteristics of the particle ignition process would be obtained.

A strength of 10% coal-gas in air was first tried, the supply being taken from the laboratory main, and the mixture made up as already described. The first sphere used was one of platinum, 4 mm. in diameter, No.6 in Table IV. Using nickel-chrome alloy heating elements on the quartz tube, ignitions of the gas mixture in the apparatus were readily obtained. It was found that at certain temperatures the ball caused ignition, and that at others it did not, and that there was apparently a certain minimum temperature below which ignition would not take place. Moreover a very sharp division was observable at this temperature, since in this particular case 880°C and 885°C gave repeated

ignitions while 870°C repeatedly failed to ignite, so that it was quite possible to specify 875°C as the minimum sphere temperature required to ignite the gas. This sharpness testifies to the accuracy of the apparatus, since it implies that the experimental scatter in the neighbourhood of the minimum igniting point where the probability of ignition may be defined as ½, is very small. Actually 875°C was observed to give roughly 50% ignitions. The sharpness of the ignition point is well shown in the results in Table IV.

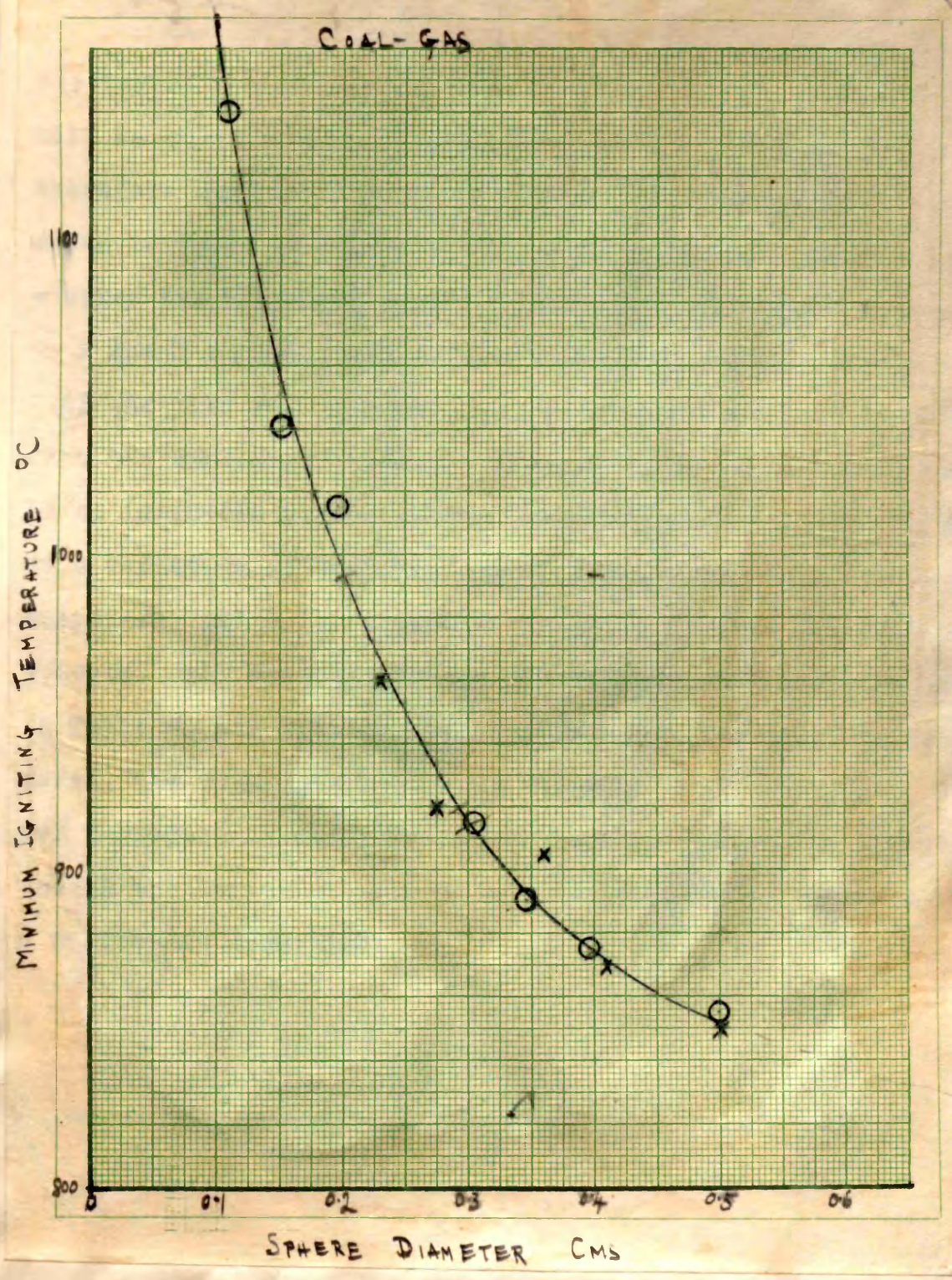
Having found such an interesting point for one sphere, we proceeded to investigate platinum spheres of different diameter Six others were used, the results being given in Table IV. In every case a sharp minimum igniting temperature is found, which is, however, different for spheres of different diameter. The smaller the sphere, the higher is the minimum temperature required for ignition. The variation is clearly seen in ~~Graph I~~ Figure 3 where the circles represent the points in Table IV, minimum igniting temperature - which we shall call the "ignition point" - being plotted against sphere diameter. It is of interest to compare our results for the larger spheres with McDavid's result (see p. 14) of 878° for the "instantaneous" ignition temperature of coal-gas.

TABLE IV.

Platinum Spheres - 10% Coal Gas.

Particle No.	1		2		3		4		5		6		7	
Diameter in cms.	.109		.151		.197		.303		.349		.398		.500	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	1250	+	990	-	1080	+	945	+	920	+	905	+	940	+
	1240	+	1005	-	1025	+	915	-	895	-	875	-	905	+
	1200	+	1025	-	985	-	955	-	915	+	890	+	890	+
	1160	+	1050	+	1040	+	940	+	905	-	885	+	875	+
	1090	-	1065	+	1025	+	925	+	920	+	880	+	855	+
	1130	-	1045	+	1005	-	915	+	915	+	880	-	845	-
	1140	-	1040	+	1025	+	900	-	905	+	875	+	870	+
	1050	-	1040	+	1010	+	915	+	900	-	880	+	865	+
	1100	-	1020	-	1000	-	905	-	890	+	865	-	840	-
	1120	-	1025	-	1015	+	915	+	895	+	885	+	840	-
	1270	+	1030	-	1010	-	910	-	890	+	870	-	850	-
	1230	+	"	"	1025	+	"	"	885	-	"	"	860	+
	1200	+	"	"	1000	-	"	"	895	-	"	"	850	-
	1160	+	"	"	1010	+	"	"	900	+	"	"	855	+
	1130	-	"	"	"	"	"	"	890	+				
	1140	-	"	"	"	"	"	"	885	-				
	1170	+	"	"	"	"	"	"	890	-				
	1160	+	"	"	"	"	"	"	895	+				
	1150	+												
	1145	+												
	1140	+												
	1130	-												
	1150	+												
Ignition Point:	1140		1040		1015		915		890		875		855	

Fig. 3.


COAL-GAS
MINIMUM IGNITING TEMPERATURE °C
1100
1000
900
800
0
0·1
0·2
0·3
0·4
0·5
0·6
SPHERE DIAMETER CMS

Note on the Cooling of Particles.

The rate of cooling of the spheres in moving from the heated portion of the quartz tube into the cold gas mixture will be greater for the smaller spheres. It appeared possible therefore that some of the difference in the ignition temperatures shown in Table IV might be due to this factor. To ascertain whether the different rates of cooling influenced the observations to a great extent, experiments were repeated for the spheres of 1.51 and 3.98 mm. diameter, shooting them from various distances from the explosion chamber. If cooling is sufficiently rapid to be an important factor in our observations, it should be shown by a variation of observed ignition point with the distance traversed, and this variation should be greater for smaller spheres. The results for the two spheres mentioned are given in Table V, and show no appreciable variation with distance moved, the apparatus not being accurate to 5^{o} in 1000^{o}. It can therefore be taken that each particle, whatever its size enters the explosion chamber at the temperature observed, to a sufficient approximation.

TABLE V.

Ignitions from different distances.

	Platinum Sphere No.2.				Platinum Sphere No.6.			
	Distance 26 cm.		Distance 11 cm.		Distance 24 cm.		Distance 10 cm.	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	1040	-	955	-	925	+	908	+
	1055	+	990	-	935	+	875	-
	1050	-	1005	-	875	-	890	+
	1045	+	1025	-	905	+	885	+
	1050	+	1050	+	895	+	880	+
	1040	-	1065	+	890	+	880	-
	1040	+	1045	+	880	+	875	+
	1025	-	1040	+	865	-	880	+
			1040	+	875	-	865	-
			1020	-	875	-	885	+
			1025	-	885	+	870	-
			1030	-	875	-		
					880	+		
					885	+		
Ignition Point:	1040		1035		880		875	

Experiments with Quartz Spheres.

The above results show clearly the importance of the size of a particle of given material in determining the point at which it will ignite a coal-gas air mixture. It was now decided to investigate the effect of using a different material. The specific heat of platinum is fairly small, 0.032 cals/gm. (from International Critical Tables, Vol. 5, p.93), so as a contrast we chose quartz (in the form of fused silica) for our second set of experiments. The specific heat of these spheres is then about 0.28 cals/gm. (from International Critical Tables, Vol. 5, p. 105). Platinum and quartz also represent a contrast in thermal conductivity, the values being roughly 0.17 and 0.03 cals/sec/deg.cent. (from data given by Kaye and Laby[20]). These values of the specific heat and thermal conductivities have been calculated for a temperature of 1000° from the data given in the references, extrapolated where necessary.

The quartz spheres were obtained in the same range of sizes as those of platinum. The experiments were performed exactly as before, with the results given in Table VI. In ~~Graph 1~~ Figure 3, the curve was drawn with reference to the circles showing the platinum results. The ignition points found for quartz have been added and are indicated by crosses. The agreement with the platinum results is indeed striking, the points lying practically on the same curve. This result was somewhat unexpected, since it is clear from the specific heats given above that a quartz sphere possesses between 8 and 9 times as much heat as a platinum sphere of the same size at the same temperature. Hence the platinum sphere can ignite the

TABLE VI.

Quartz Spheres - 10% Coal-Gas.

Particle No.	1		2		3		4		5	
Diameter in cms.	0.23		0.275		0.36		0.41		0.5	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	925	-	975	+	900	+	815	-	910	+
	940	-	945	+	885	-	915	+	880	+
	980	+	935	+	880	-	900	+	855	+
	960	-	920	+	890	-	890	+	825	-
	1000	+	915	-	900	-	875	+	850	+
	980	+	925	+	905	+	870	+	835	-
	970	+	920	+	915	+	865	-	855	+
	975	+	915	+	920	+	860	-	840	-
	960	+	900	-	900	-	860	-		
	955	+	895	-			870	+		
	945	-	905	-						
	940	-	915	-						
	945	-	925	-						
			945	+						
			925	+						
			915	-						
Ignition Point.	960		920		905		870		850	

mixture with only $^1/_8$th of the heat required in quartz, if the size and temperature are the same. The size and the temperature are therefore apparently the fundamental factors in the particle ignition process, the total energy content playing a very subordinate part. Further proof of this fact will be given in Part III and its importance in connection with the theory of the process discussed.

(c) Experiments with Pentane. The results of the coal-gas experiments suggest the possibility of obtaining definite information of great interest. The apparatus has shown itself capable of determining a definite ignition point with reasonable accuracy. The composite nature of coal-gas however renders results obtained for it mainly of qualitative value. The curve appears at first sight to be asymptotic for increasing diameter. If this type of curve is a general feature of particle ignition in gases, it becomes of interest to see how the sphere igniting temperatures compare with the "ignition temperature" of the gas mixture as found by the usual methods discussed in Part I. Experiments similar to those with coal-gas are therefore required for a single combustible gas, whose ignition temperature under ordinary conditions is well-known.

We therefore again tried to obtain ignitions of methane-air mixtures, this time using platinum heating elements. These also burnt out readily at the required temperatures, and the hope of obtaining for methane a set of results similar to those for coal-gas had to be abandoned. We did actually manage to ignite a 7% methane in air mixture by using a larger platinum sphere. The ignition point

for a sphere 6.5 mm. diameter was about 1200°C.

Pentane was chosen in place of Methane, since Mason and Wheeler's results (p. \\) indicate it to be much more readily ignitable. We commenced with a mixture which contained 3% pentane in air, made up by allowing the required volume of pentane to evaporate from the liquid into the gas holder. The experimental procedure was exactly as before. The results obtained with platinum spheres are shown in Table VII.

TABLE VII.

Platinum Spheres - 3% Pentane.

Particle No.	1		3		4		6		7		8	
Diameter in cms.	0.109		0.197		0.303		0.398		0.500		0.550	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	1220	-	1200	-	1165	+	1085	+	1075	+	990	-
	1275	-	1190	-	1120	-	1035	-	1035	+	1025	+
	1325	-	1240	+	1155	-	1075	+	1025	-	985	-
	1400	+	1220	-	1170	+	1060	+	1035	-	1015	+
	1365	+	1220	-	1140	-	1050	-	1065	+	1005	-
	1400	+	1285	+	1150	+	1045	-	1055	+	1025	+
	1400	+	1265	+	1135	-	1060	-	1025	-	1020	+
	1365	-	1250	+	1150	+	1075	+	1045	+	995	-
			1220	-	1120	-	1050	-	1015	-	1005	+
			1260	+	1170	+	1070	+	1075	+		
			1230	-	1140	-	1035	-	1050	+		
			1270	+	1150	-	1050	-	1045	+		
					1170	+	1060	-	1025	-		
							1075	+	1035	-		
							1070	+	1045	+		
							1055	-	1050	+		
									1005	-		
Ignition Point	1370		1240		1155		1065		1040		1005	

~~Further experiments were again made with quartz spheres, the results of these being given in Table~~

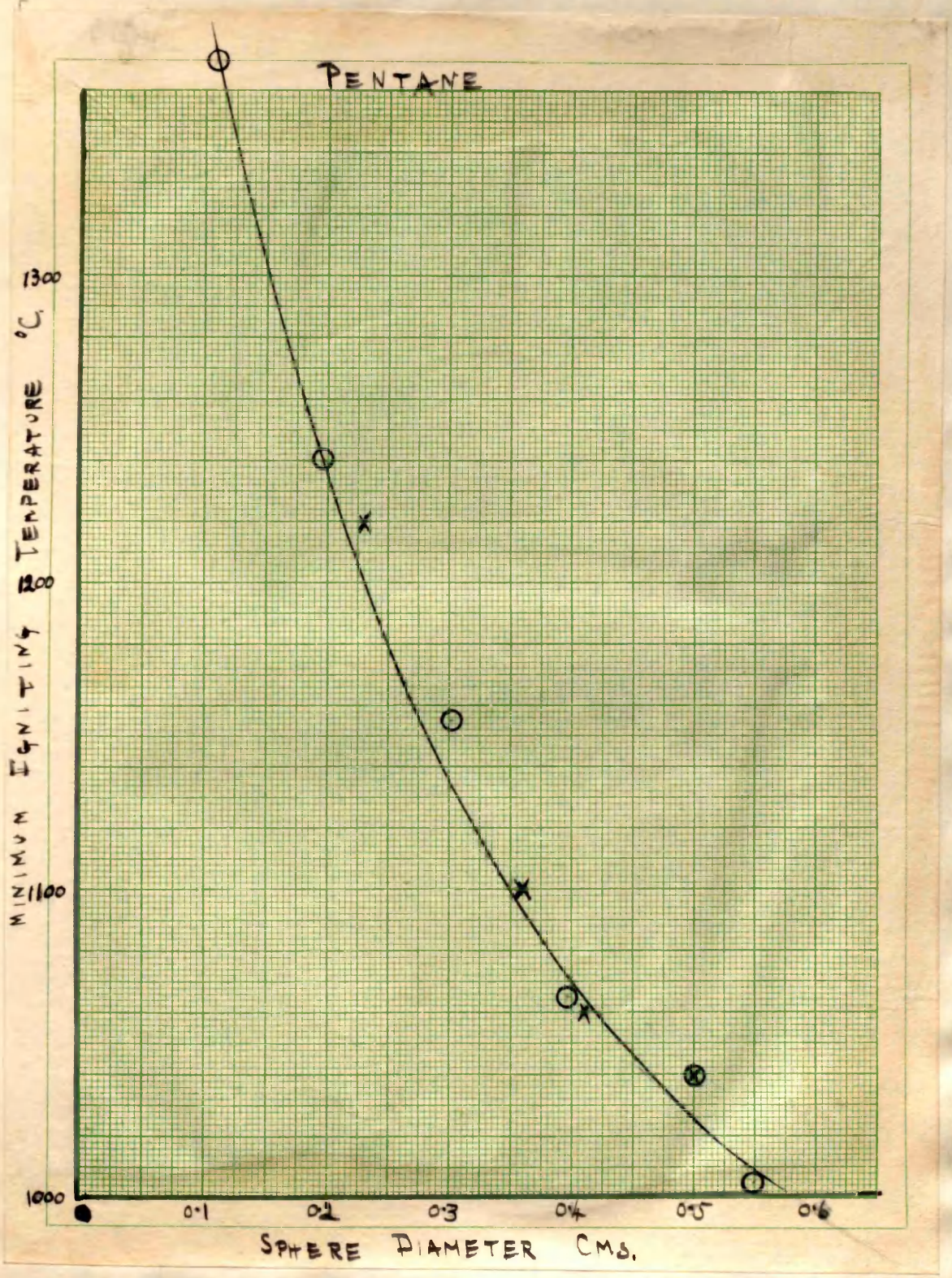
As for coal-gas, definite minimum igniting points appear for the different particles, the temperatures increasing rapidly as the size diminishes. Further experiments with quartz spheres were again made, the results being given in Table VIII.

TABLE VIII.

Quartz Spheres - 3% Pentane.

Particle No.	1		3		4		5	
Diameter in cms.	0.23		0.360		0.41		0.5	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	1300	+	1190	+	1050	-	1070	+
	1260	+	1150	+	1075	+	1050	+
	1190	-	1120	+	1060	+	1030	-
	1250	+	1090	-	1050	-	1050	+
	1230	+	1115	+	1060	+	1060	+
	1220	+	1085	-	1045	-	1035	+
	1150	-	1115	+	1060	-	1055	+
	1220	-	1110	+	1080	+	1025	-
	1230	+	1100	+	1025	-	1030	-
	1210	-	1080	-	1080	+	1050	+
	1240	+	1085	-	1055	-	1035	-
			1090	-	1060	-	1045	+
			1100	-	1060	+	1045	+
			1135	+	1075	+	1045	-
							1020	-
							1035	-
							1045	+
Ignition Point.	1220		1100		1060		1040	

Fig. 4.


PENTANE
MINIMUM IGNITING TEMPERATURE °C.
1300
1200
1100
1000
0·1
0·2
0·3
0·4
0·5
0·6
SPHERE DIAMETER CMS.

Tables VII and VIII show that within the limits of accuracy of the method the igniting points of the quartz spheres are not appreciably different from those of platinum spheres of the same diameter. The agreement is again illustrated in ~~Graph 2~~ Figure 4, where circles again represent platinum and the crosses, quartz, the curve being drawn first with reference to the circles. Once again size seems to be a more dominant factor than material in determining the igniting point of a sphere.

(d) Experiments with Hydrogen.

The above results for pentane show that the minimum temperatures at which the spheres will ignite the mixture are mugh higher than the usual "ignition temperatures" of the mixture as determined by common methods. Thus the curve has only a small gradient at about 1000°C when the sphere diameter is 5½ mm., while the ignition temperature for a 3% mixture is about 515°C (cf. Table III, p. 11). It was therefore decided to perform a similar set of experiments, using hydrogen-air mixtures, to see whether the feature of a minimum igniting temperature higher than the ignition temperature still obtained, and, if so, if it occurred to the same extent.

The hydrogen was obtained from a cylinder, supplied by the British Oxygen Co. The mixture investigated was one of 20% hydrogen in air. Experimental procedure being exactly as in the previous work, the results for platinum spheres are given in Table IX and for quartz in Table X.

TABLE IX.

Platinum Spheres - 20% Hydrogen.

Particle No.	3		3a		4		7		8	
Diameter in cms.	0.197		0.240		0.303		0.500		0.550	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	880	-	915	+	915	+	930	+	855	+
	935	+	885	+	870	+	800	-	800	+
	885	-	845	-	855	-	810	-	745	-
	900	-	855	-	865	+	810	+	785	-
	920	-	885	+	875	+	840	+	805	+
	975	+	880	+	845	+	825	+	790	+
	940	+	870	-	825	-	810	-	780	-
	915	-	890	+	835	+	825	+	810	+
	905	-	875	-	845	+	820	+	785	-
	960	+			835	+	810	+	795	+
	945	+			820	-	805	-	790	-
	925	-			835	-	820	+		
					855	+	800	-		
					840	-	805	+		
							815	+		
							810	+		
Ignition Point.	930		880		840		810		795°C	

TABLE X.

Quartz Spheres - 20% Hydrogen.

Particle No.	1a		2a		3		4		5	
Diameter in cms.	0.170		0.257		0.360		0.410		0.500	
	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.	Temp.	Obs.
	965	+	865	+	900	+	835	+	780	-
	885	-	845	+	875	+	790	-	820	+
	930	+	800	-	850	+	825	+	805	+
	910	-	820	-	810	-	820	+	800	+
	915	-	825	-	835	+	800	-	795	-
	935	+	835	-	825	+	805	-	820	+
	925	-	840	-	815	-	810	+	790	-
	925	-	860	+	820	-	800	-	810	+
	940	+	850	+	830	+	815	+	800	+
	940	+	840	+						
Ignition Point.	930		840		825		810		800	

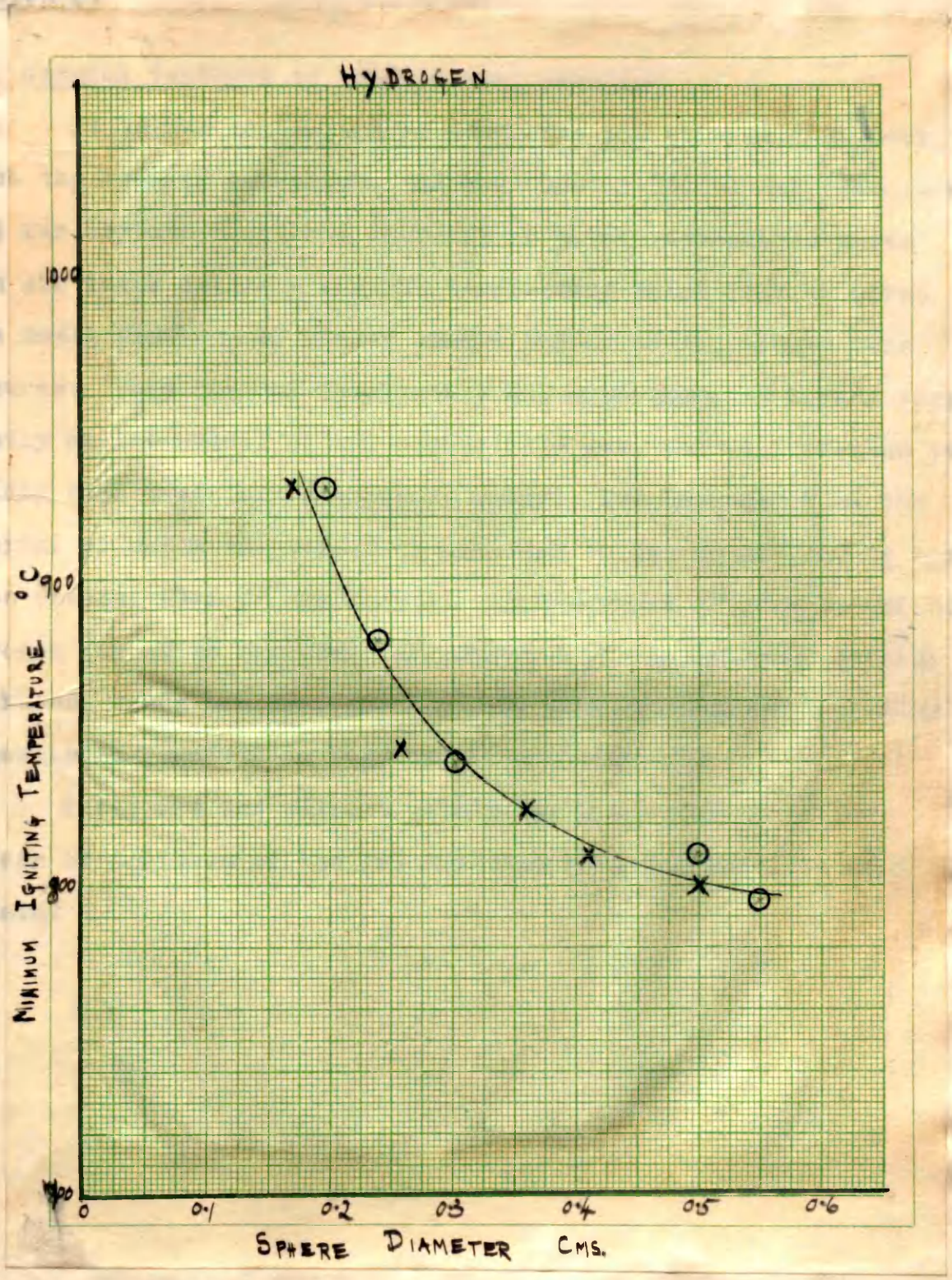
When the igniting points in the hydrogen experiments are plotted against diameter of sphere as in Fig. 5, it is seen that the quartz temperatures do not coincide so closely with the platinum temperatures for the same diameter, as was the case with coal-gas and with pentane. The difference is now noticeable but is still not very great, and is prominent only for the smaller spheres.

Figure 5

~~Graph 3~~ shows the igniting points found in the hydrogen experiments plotted similarly to those for coal-gas and for pentane. The quartz temperatures in this case do not coincide quite so closely with the platinum temperatures for the same diameter. The difference is still not very great, but becomes noticeable for the smaller spheres.

Now the ignition temperature of a 20% hydrogen-air mixture is about 590°C.[12]. Hence, as already found for pentane, spheres in the range of size used require to be at a temperature considerably higher than the ignition temperature of the mixture, before they will cause ignition. The excess required is not however so great proportionally for hydrogen as it is for pentane.

Fig. 5.


HYDROGEN
1000
900
800
700
MINIMUM IGNITING TEMPERATURE °C
0
0·1
0·2
0·3
0·4
0·5
0·6
SPHERE DIAMETER CMS.

Section 5.

General features of experimental Results.

It is now convenient to summarise the general phenomena which the results establish. In the first place it has been shewn that for certain ignitable mixtures of given combustible gases with air there exists a minimum temperature which must be given to a small platinum or quartz sphere before it can ignite such mixtures. This minimum temperature has been shewn to depend very greatly on the nature of the combustible gas, and it increases very rapidly with diminishing sizes of sphere, but dependence on the material of which the sphere is composed is not marked and in most cases investigated is negligible. In the cases of pentane and of hydrogen for which ignition temperatures by the ordinary methods are known, these are considerably less than the minimum igniting temperatures required in even the largest spheres.

These are the salient points which any theory of the process of ignition of the gas mixtures by a hot particle must explain.

PART III. THE THEORY OF IGNITION BY HEATED SPHERES.

PART III.

Section 1.

Introduction - Difficulties in accounting for the observed results.

The experimental results which have been obtained for pentane, hydrogen, and coal-gas, show from the similar shapes of curves representing the relation between minimum igniting temperature and size, that some definite process occurs when a hot particle ignites a gas, and that some definite requirements are fulfilled. Two simple limiting conditions at once suggest themselves (a) that the total amount of heat required to ignite the gas is a constant, and (b) that the initial rate of heat supply to the gas must reach a certain constant value. The condition (a) is readily seen not to function as the limit requirement, since we have already shown in Part II that a platinum sphere contains roughly only $^1/8$th of the heat in a quartz sphere of the same size. Moreover, for a given sphere material, it requires that Td^3 = constant where T is the minimum igniting temperature and d is the diameter. The two values of Td^3 for the 0.55 mm. and 0.109 mm. spheres with pentane are respectively 167 and 1.78 so that the smallest sphere can ignite the gas mixture with roughly only $\frac{1}{100}$th of the heat required in the largest. The second suggested condition (b) is dependent on the area of the sphere surface, and requires that Td^2 = constant. The values of this quantity corresponding to those of Td^3 above are respectively 304 and 16.3. Thus the larger sphere requires to have an initial rate of heat supply to the gas

nearly 20 times that of the small one. Neither of the simple conditions (a) and (b) can therefore account for the observed results, and it is clear that the small spheres have a very much greater "efficiency" of ignition, expressed in terms of heat required, and the phenomena must be considered much more carefully if we are to account for the results obtained.

Taylor-Jones, Morgan, and Wheeler[13] put forward a theory according to which ignition requires the attainment of the ignition temperature in a certain minimum volume of the gas. In order to test this theory, as applied to particle ignition, it is necessary to know the temperature distribution produced in the gas by the sphere. This is, in itself, an exceedingly complex problem which has nowhere been investigated experimentally, nor has an exact mathematical solution from heat conduction theory been given. However in an attempt to apply the ignition theory of Taylor-Jones, Morgan, and Wheeler, we examined the temperature distribution problem thoroughly. Eventually it was found possible to derive a solution which may be assumed as a reasonable approximation to the temperature distribution in a gas surrounding a stationary solid sphere. An account of this work is presented as an Appendix to this thesis.

One form of solution derived for the gas temperature at radius r is

$$\theta = \frac{T_o}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{r-a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx + \frac{T_o}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{r+a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx, \quad r>a$$

Where T_o is twice the sphere temperature, and a is the radius of the sphere.

In the appendix, graphs are given which illustrate the distribution given by the above expression for various times, for spheres of diameter 0.5 and 0.2 cms. Now, consider the pentane results. If the theory of Taylor-Jones, Morgan, and Wheeler is applicable, the gas volumes which are raised to 515°C by the 0.5 cm. diameter sphere at 1040°C and by the 0.2 cm. diameter sphere at 1240°C in the same short time should be equal. These volumes can be ascertained from the graphs in the appendix, and it may readily be shown that they are respectively approximately 0.004 c.c's and 0.0008 c.c's i.e. one is five times the other, for t = .001 secs. With increasing time the ratio increases slightly.

These considerations show that the theory of Taylor-Jones, Morgan, and Wheeler breaks down when applied to the present case. This form of simple thermal theory cannot therefore explain the ignition characteristics of hot spheres. In order to do so we have found it necessary to consider the gas reaction more fundamentally. We proceed now to a short discussion on general ignition theory which serves to introduce the theory of hot particle ignition which is advanced in this thesis, and in the light of which its importance can be realised.

Section 2.

General Considerations on Thermal and Chain Explosions in Gases.

The inflammation of gaseous mixtures has been the subject of numerous investigations during recent years. As a result it is generally accepted that there are two distinct mechanism by which explosion of gas mixtures can take place. In an ignitable mixture at temperature $T^{o}K$ the Maxwell distribution law indicates that the number of molecules with energy greater than a value E, is proportional to $e^{\frac{-E}{RT}}$, e being the Napierian base, and R the gas constant. Now the theory of chemical reactions in the gas phase assumes that only molecules with energies greater than a certain energy A can react. A is called the activation energy of the reaction, and the number of molecules which can react is then proportional to $e^{\frac{-A}{RT}}$. The number of molecules capable of reaction therefore increases very rapidly with temperature if A is positive, as it is in most cases. From these considerations, we see that the velocity of reaction at a temperature T is also proportional to $e^{\frac{-A}{RT}}$, and therefore also increases rapidly with temperature. Since the gas combustions involved in explosion are exothermic, this means that the higher the temperature, the more quickly does the mixture generate heat. In general, heat is also lost from the system to the surroundings. For normal temperatures the number of molecules capable of reaction is exceedingly small, because of high values of A, and the rate of heat production is quite insufficient to overcome the loss to the surroundings. But for a

sufficiently high temperature the heat of reaction will be produced rapidly enough to compensate for heat loss, and the gas temperature will therefore rise further. The velocity of reaction is thereby continually accelerated and will be observed as explosion.

The fulfilment of the heat balance condition represents therefore one possible mechanism of explosion. Such explosions are called thermal, from their nature. The theory of Taylor-Jones, Morgan, and Wheeler already mentioned is essentially of this type but is defined with reference to the ignition temperature. The reason for its breakdown is then apparent, in that the above argument shows the "ignition temperature" as generally determined to be itself dependent on the relation between velocity of reaction and rate of heat loss in the particular apparatus in which the determinations are made. It cannot therefore be used as a fundamental in ignition theory. To give an adequate theory of any thermal gas explosion it therefore becomes necessary to consider the heat production and heat loss conditions prevailing in the particular circumstances.

This is not however the only type of explosion which can occur in gases. The theory of chain reactions shows that what is called a purely chain explosion can take place. Chain theory presupposes that on reaction, intermediate molecules are formed with very high energies derived from the heat of reaction, and that these can impart energy, by collision, to the molecules of the reacting gases. This implies that the number of molecules with energy E becomes greater than that given by the simple Maxwell

distribution formula. The energies imparted by reaction products may then be sufficient to activate the recipient molecules and so a new source of activation arises. The number of secondary activations arising from one initial centre of reaction is called the length of the chain. The mathematical theory of such reactions is extensively discussed by Semenoff[14]. He shows that in principle branching chains may occur, and that under suitable conditions of molecular concentration and with sufficiently exothermic reactions, the length of chain may become infinite. This will clearly be observed macroscopically as explosion. His theory shows, that if the chains have no mutual action, the conditions for such an explosion to occur are independent of the number of initial centres. When mutual action between the chains occurs, this simple theory requires to be modified. If f is the probability of branching of the chains, and g the probability of their rupture, the equation for the stationary state of the reaction is

$$n_0 + (f-g)n = 0 \qquad \ldots\ldots\ldots (1)$$

n_0 being the number of active centres generated uniformly per unit volume per unit time by thermal motion or other agency outside the chain production, and n is the total number of active centres per unit volume at the instant. Semenoff discusses a number of cases of mutual action of the chains. In particular, when the branching is dependent on mutual action, but the rupture is not, we may put $f = f_0 n$. This is the most favourable set of circumstances for

explosion. Equation (1) now becomes

$$n_o + f_o n^2 - g n = 0 \qquad \ldots\ldots\ldots (2)$$

If $4n_o f_o \geq g^2$, the stationary reaction is thus impossible, n becoming imaginary. The reaction is now self-accelerated to explosion, the condition involving n_o, the number of active centres generated per unit time, so that the elementary simplicity is no longer tenable.

The above short account of the two generally accepted theories of gas ignition has been required in order to show how it is possible to state definitely the class of explosion obtained in our experiments. We now proceed to show that the explosions observed by us come into the first category, i.e. are thermal explosions.

Section 3.

The Classification of the Observed Explosions.

It is now more or less agreed that all gaseous oxidations proceed with a chain mechanism (cf. Semenoff[15]), the reaction taking place at measurable slow rate unless one or other of the above types of explosion can take place. The first act of a hot sphere when introduced into a gas mixture will be the production of initial centres, the number of which will be proportional to the surface area. Now, suppose that the mutual action of the chains happens to be such that the most favourable set of conditions for chain explosion, as defined in equation (2), obtain. Then in the expression $4 n_0 f_0 \geq g^2$, both sides are functions of temperature and pressure, since f_0 and g are both dependent on these quantities, and since, moreover, n_0 is of the form $Ae^{-\frac{E}{RT}}$. In applying this discussion to the present work, we know that the condition $4 n_0 f_0 \geq g^2$ was not fulfilled with the gas mixtures at room temperature and at atmospheric pressure, since they did not explode. The introduction of a hot sphere can alter the quantities n_0, f_0 and g only by raising the gas temperature. These quantities will therefore vary from shell to shell, according to the temperature distribution. It follows that under such circumstances the conditions for even a chain explosion lead back to a thermal conductivity problem: n_0, f_0 and g are varying radially, and the condition that for explosion to take place $4 n_0 f_0 \geq g^2$ must be satisfied in shell after shell leads to some heat balance condition which simply defines the temperature which must be maintained.

It is suggested that the preceding paragraph throws new light on the general relationship between chain reaction and explosion, and thermal explosion.

Secondly, if we can assume that the mutual action of the chains is negligible, the self acceleration to a purely chain explosion is independent of the number of initial centres, but can only take place between an upper and a lower pressure limit. These limits depend on the temperature. Hinshelwood and Gibson[16] have shown for oxygen and hydrogen that the upper limit rises with temperature, and give it as 700 mm. for 576°C., while Sagulin, Kowalsky, and Semenoff[17] show that the addition of nitrogen lowers it. The mixtures used in our experiments were therefore well above any threshold for pure chain explosion to take place by a kind of trigger action of the hot ball. Even if they had not been, the variation of ignition point with size of sphere shows definitely that a purely chain explosion independent of the number of initial centres created is not occurring. Hence even if the effect of mutual action of the reaction chains in the gases used is negligible, the experiments were conducted in a region where the chain reaction was stationary. The explosions must therefore involve acceleration of local reaction to a state where rate of heat production is greater than rate of heat loss, i.e. the explosions observed must be of the thermal type.

Section 4.

The Theory of the Ignition Process.

In the preceding section it has been shown that the ignitions observed in our experiments are probably determined by some heat balance condition. In the following theory, the simplest possible assumptions are used to define that condition, and by the treatment which is given, we are able to derive an expression for the minimum temperature T at which a sphere of radius a will ignite a given gas mixture.

For simplicity we deal only with a stationary sphere, and the first problem presented is that of the temperature distribution produced in the gas round the sphere by conduction, neglecting convection movements. It was originally hoped that the approximation derived in the appendix, for the case of a non-burning gas, might be developed by superimposing the effect of combustion. This hope had to be abandoned. It will not be out of place, however, to give the derivation of the simplest differential equation for the heat-flow in the burning gas, although we have been unable to obtain a solution.

For a non-burning uniform medium the Fourier equation for spherically symmetrical temperature distribution is

$$\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r} = \frac{1}{k}\frac{\partial\theta}{\partial t} \qquad \ldots\ldots\ldots (3)$$

where k is the thermometric conductivity, whose variation with temperature is here neglected. But in the case of a combustible

gas mixture, when we consider the heat-content of the thin shell between radii r and r + dr we must allow for combustion proceeding at a velocity appropriate to the temperature θ in the shell. If V is the fraction of unit volume of mixture which would react per second, and if Q is the amount of heat produced by the burning of unit volume of the mixture, heat is produced by combustion in the shell at rate $4\pi r^2 V_\theta Q dr$. The Fourier equation is therefore replaced by

$$K\left(\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r}\right) + V_\theta Q = C\frac{\partial\theta}{\partial t}$$

or

$$\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r} = \frac{1}{k}\frac{\partial\theta}{\partial t} - \frac{V_\theta Q}{K} \qquad \text{.....(4)}$$

Chemical kinetics show that V_θ depends on the concentration of the reacting substances in a manner determined by the molecular order of the reaction, and on temperature approximately in the exponential fashion indicated by the Arrhenius equation for the velocity constant m of the reaction, i.e., $m = Ce^{\frac{-A}{R\theta}}$, where C and A are constants, A being the energy of activation of the reaction, and θ is the absolute temperature. If we neglect the variation with concentration, which we may do for our purpose since we are concerned only with initial stages in the ignition, we obtain the simplest form of the differential equation as

$$\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r} = \frac{1}{k}\frac{\partial\theta}{\partial t} - \alpha e^{-\frac{\beta}{\theta}} \qquad \text{.....(5)}$$

where α and β are constants.

Since we have failed to find a solution of equation (5), we turn to the following convenient treatment. It is in general undoubtedly inexact, since by leaving out the differential equation we are considering only a shell at the surface of the sphere, and ignoring the effect of the heat passing out from it on the outer regions. But it may be the best possible theoretical attack on the problem, since questions of adsorption and accommodation coefficient effects might in any case vitiate the application of the exact solution of equation (5).

Let us assume

(a) that the layer of gas immediately in contact with the surface is raised instantaneously to the sphere surface temperature T;

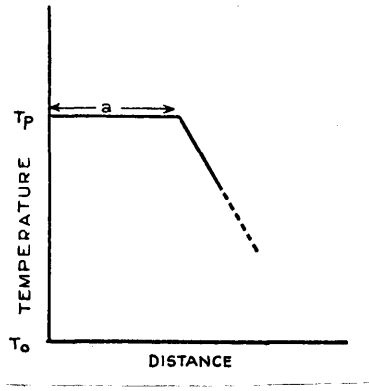
(b) that the rate of loss of heat per unit area of the sphere surface is proportional to the difference between its temperature T and the initial temperature T_o (room temperature) of the gas, i.e., is $p(T - T_o)$, where p is a constant;

(c) that this gradient is uniform throughout the thin shell of gas instantaneously heated round the surface.

If these assumptions are permitted, we are picturing a distribution of temperature of the form of fig. 6.

Now we assume that extinction of initial combustion is caused by too rapid loss of heat into the unburnt portions of the gas mixture. Then, considering the shell dr round the sphere surface, heat will flow into it by conduction at rate $4\pi a^2 p(T-T_o)$

Fig. 6.



while heat is also lost by conduction away from the outer surface at rate $4\pi(a + dr)^2 p(T - T_0)$. Hence, if we neglect the square of dr, we have a net loss from the shell at rate $8\pi a k(T - T_0)dr$. Meanwhile heat has begun to be produced by combustion, and, since in the initial stages, neglecting variation in concentration of the reacting gases, we can put the fraction of unit volume of mixture reacting per second as $V_\theta = \alpha k_\theta$, where α is the concentration factor and k_θ the velocity constant. Assuming the Arrhenius equation, we have $k_\theta = C e^{-\frac{A}{R\theta}}$ where θ is the absolute temperature. Hence the initial rate of heat production in the shell is

$$4\pi a^2 dr\, V_T Q = 4\pi a^2 dr.\, Q\beta e^{-\frac{A}{RT}}$$

where β includes the concentration factor and the C of the Arrhenius equation.

Now it may be assumed that if this initial rate of heat production is greater than the above rate of heat loss by conduction, the temperature of the shell will rise, heating outer portions, and so combustion will spread throughout the gas mixture. If it is less, the shell will cool and we may consider extinction to take place. The first case will give explosion, the second will not. When the two are equal, the equality should define a limiting temperature for explosion, and this equality should be satisfied by the minimum temperature at which the sphere of radius will ignite the gas mixture. On equating them we find, the temperatures being on the absolute scale,

$$8\pi a p(T-T_0)\,dt = 4\pi a^2\,dt \cdot Q\beta e^{-\frac{A}{RT}} \quad \ldots\ldots\ldots (6)$$

$$\therefore \quad \frac{2p}{a}(T-T_0) = \beta Q e^{-\frac{A}{RT}}$$

$$\therefore \quad \log \frac{2p(T-T_0)}{\beta Q a} = -\frac{A}{RT}$$

$$\therefore \quad \log \frac{T-T_0}{a} = \log \frac{\beta Q}{2p} - \frac{A}{RT} \quad \ldots\ldots\ldots (7)$$

or we may express a in terms of T as follows:

$$a = \frac{2p}{\beta Q}(T-T_0)\, e^{\frac{A}{RT}} \quad \ldots\ldots\ldots (8)$$

The theory thus leads to a relationship between sphere radius and sphere temperature which is satisfied when explosion only just takes place. Hence T in equation (8) is the minimum temperature at which a sphere of radius a will ignite a certain gas mixture. The gas mixture in question is characterized by the constant βQ, while the material of the sphere is involved in the constant p, since it defines the heat exchange between the surface and the gas. It is thus at present out of the question to test the validity of this expression by direct calculation and comparison with the foregoing experimental results, since the constant p is unknown, and in most cases so also are A and β, which are derived from the kinetic equation of the reaction.

The validity of the expression may however be tested indirectly. There are certain elementary properties which it must have. Thus it ought at least to give a curve of the same general

form as those shown in figures 3–5 for the variation of T with a and it may readily be shown by taking values of A, β, p and Q of the correct order that it does actually do so. Figure 7 shows the curve obtained by calculating T for various values of a from equation (6) assuming A = 30,000 cals/gm.mol. Q = 0.50 cals/c.c., $\beta = 10^{10}$ p = 10 cals/sq.cm./°C/sec. These values of A and β are the correct order and correct dimensions (cf. Hinshelwood Kinetics of Chemical Change in Gaseous Systems, second edition, Oxford 1929, page 53. He gives A = 44,000 for hydrogen iodide, and from his data there also β may be calculated to be 4.8 x 10"). The order of Q is also correct for the caloriric value or unit volumes of gas mixtures such as were used e.g. for a 3% pentane air mixture Q = 0.25 cals/c.c. assuming the reaction

$$C_5H_{12} + 6.467O_2 + 25.868N_2 \longrightarrow$$

$$0.234^{Co}{}_2 + 4.766CO + 4.766H_2$$
$$+ 1.234H_2O + 25.868N_2$$

and using the values of heat of formation given in the International Critical Tables, vol. V. The value of p is the most difficult quantity of which to obtain the order, and what has been done is to calculate it from the gradients for very small times derived by the expression

$$\theta = \frac{T_0}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{r-a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx + \frac{T_0}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{r+a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx \qquad \text{for } r >$$

obtained in the appendix for the temperature distribution in gas round a hot sphere. The result is of the order 10 cals./sq.cm./°C/sec

Fig. 7.

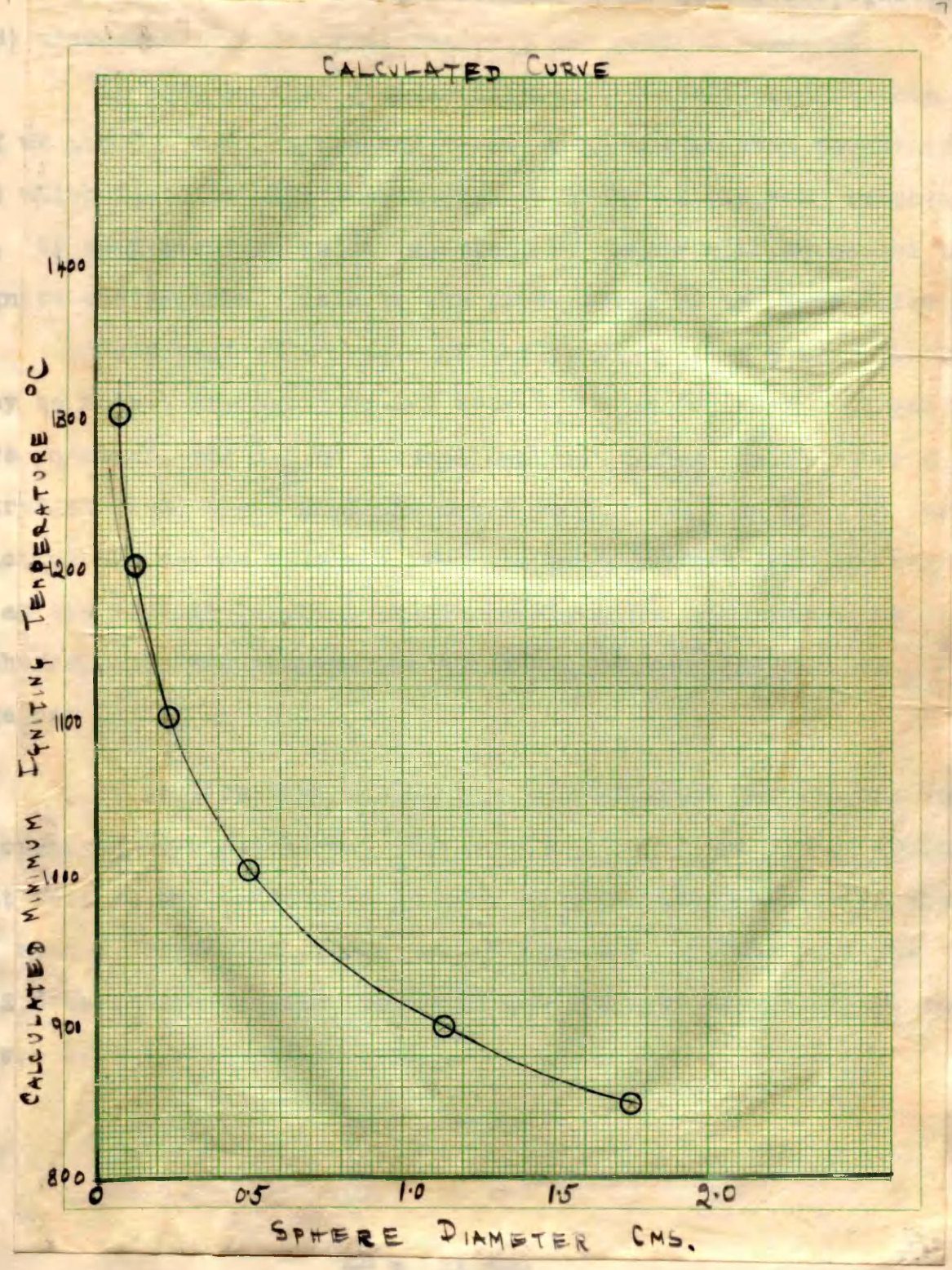

CALCULATED CURVE
CALCULATED MINIMUM IGNITING TEMPERATURE °C
1400
1300
1200
1100
1000
900
800
0
0·5
1·0
1·5
2·0
SPHERE DIAMETER CMS.

Figure 7 therefore shows that

and has been taken for p. [illegible] for correct order quantities, equation (8) ~~therefore~~ predicts qualitatively the results observed.

In another more obvious detail it fulfils requirements. If we put $T_o = T$, a becomes zero. T is the minimum temperature at which ignition will take place. Clearly if the room temperature T_o is sufficient to cause ignition, no sphere will be needed to ignite the mixture. This is the explanation of the zero value of α

More particular tests of the validity of the expression may be made. Primarily we see from equation (7) that if A and β are constant, $\log \frac{T - T_o}{a}$ plotted against $\frac{1}{T \text{ abs.}}$ should give a straight line, whose gradient would be $\frac{A}{R}$. In fig. 8 are plotted the values obtained from the experimental results, taking T as the minimum igniting points obtained for the respective spheres, and room temperature as 18°C. We have plotted $\log_{10} \frac{T - T_o}{a}$ against $\frac{10,000}{\text{abs. } T}$

It is seen that the pentane and hydrogen results lie very closely to straight lines. The coal-gas lines are not so definite but this is not unexpected in such an uncertain composition where no single activation energy can be supposed. If the suffixes 1,2,3 designate pentane, coal-gas and hydrogen respectively, the slope of the lines drawn give

$$\frac{A1}{R} = 10,470$$

$$\frac{A2}{R} = 10,790$$

$$\frac{A3}{R} = 11,510$$

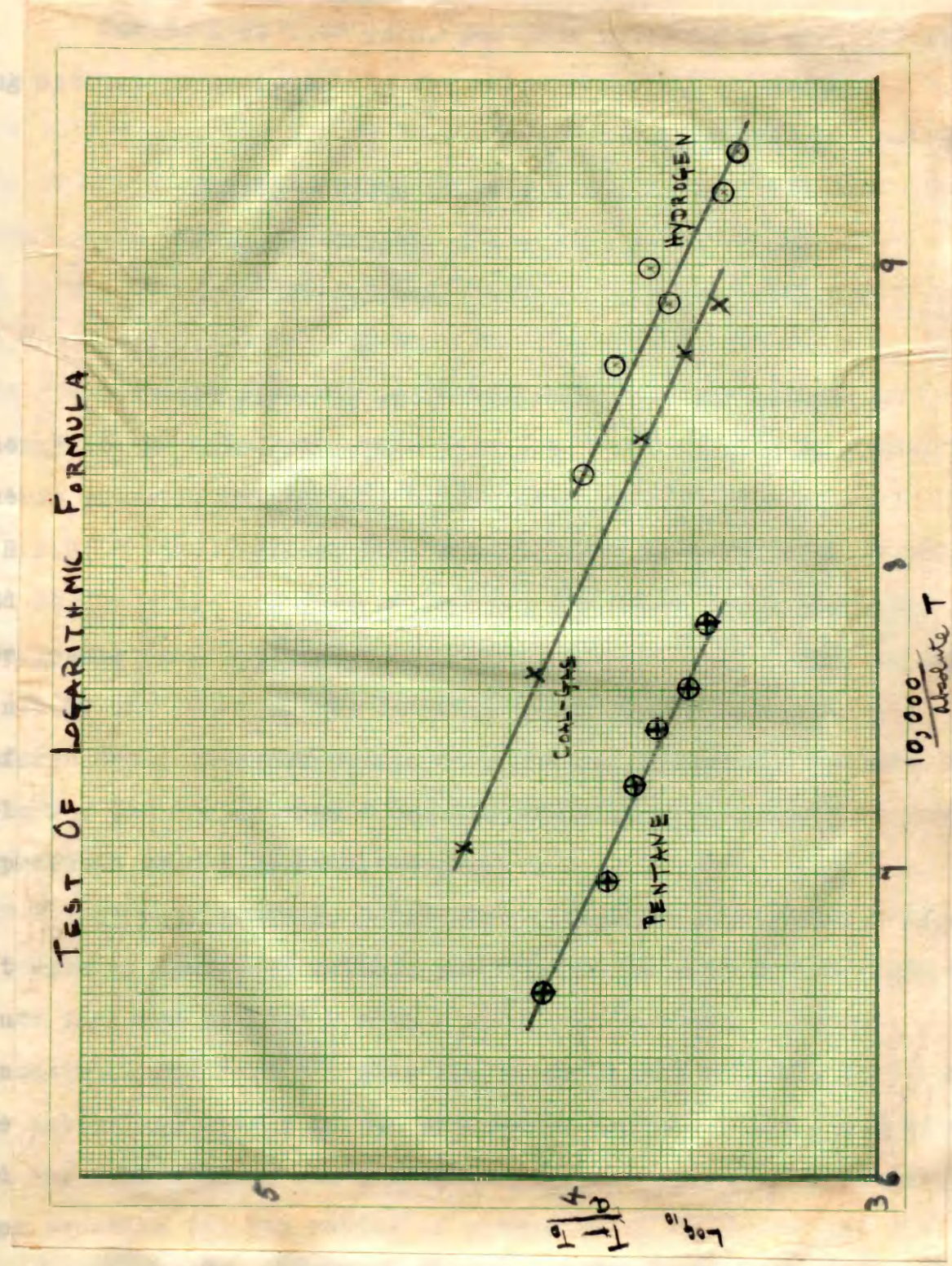

TEST OF LOGARITHMIC FORMULA
HYDROGEN
COAL-GAS
PENTANE
$\log_{10} \frac{T_1 - T_0}{\alpha_4}$
$\frac{10,000}{\text{Absolute } T}$
5
6
7
8
9

Fig. 8.

Taking R as 1.98 cals. per gram molecule we get the following activation energies for the three reactions concerned.

	Cals. per gm. molecule
Pentane-oxygen	20.700
Coal-gas-oxygen	21,400
Hydrogen-oxygen.	22,800

The most recently published value for the activation energy of the hydrogen oxygen reaction in the region of atmospheric pressure is given by N. Semenova (Acta Physicochimica U.R.S.S. 6 Jan. 1937, p. 25), who finds it to be between 21,000 and 25,000 cals. per gram molecule. The above value therefore represents very good agreement with the activation energy as determined by the study of the chemical kinetics of the reaction. Unfortunately reliable values of a similar nature are not available for pentane so that a further check on the validity of the expression cannot be attained here.

It can, however, be checked in another connection. In our attempts to ignite 7% methane air mixture we only just managed to cause ignition at 1200°C with a sphere of 6.5 mms. diameter. Hinshelwood and Fort[18] give the value 61,400 cals/gm. mol. for the activation energy of the methane oxidation. Using this value and the values of β and p used above (p.59) we can calculate from equation (6) the radius of sphere which should ignite the mixture at 1200°C. Taking $Q = 0.66$ cals/c.c. for the 7% mixture, we find $\alpha = 0.44$ cms. Considering the possibilities of errors in β and p, this represents reasonable agreement with experiment.

The theory also offers an interpretation of the remarkable equality of the igniting points for both platinum and quartz spheres The expression for the temperature in terms of the radius involves the material of the sphere only as a first approximation in the quantity p, which defines the temperature gradient near the surface. At temperatures of the order required, - the variations of p by use of a different sphere substance will be small compared with the variation of the term $e^{\frac{-A}{RT}}$, and so in experiments of no greater occurrancy than ours the effect of particle material will not be noticed. This approximate statement requires some modification with reference to the possibility of catalysis, which is given in the next section. The average value of the constant $\log \frac{\beta Q}{2p}$ may also be found from our results. For hydrogen it is 8.15 with a maximum divergence of 0.04 and for pentane it is 7.09 with a maximum divergence again of 0.04. These small divergences show the accuracy of the linear relationship. Taking p as 10 cals/sq.cm./sec./deg. and Q, for hydrogen 0.52, for pentane 0.25 cals/c.c. for the mixtures used we find $\beta = 5.4 + 10^9$ for hydrogen, and $\beta = 9.9 + 10^8$ for pentane. These quantities are of the correct order.

Section 5.

Criticism of the derived Expression.

So far we have seen that equation (8), derived from the theory which was developed to describe the particular thermol conditions determining ignition of the gas mixture by a hot sphere, succeeds exceedingly well in explaining the observed phenomena qualitatively and moreover gives good quantitative agreement when data available from other work are compared. There are however certain criticisms which may be made.

In the first place, no account has yet been taken of the possibility of catalytic action of the surface of the sphere. The general problem is of interest. The theory can be transformed to deal with it rather simply by assuming that the initial layer of combustion whose continuance determines ignition is the one in which catalysis occurs, and that it is due to a heterogeneous reaction between molecules adsorbed in the sphere surface. An expression of the same type is then derived, but the quantities β and A refer now to the combustion rate of adsorbed molecules, A being the energy of activation of the heterogeneous reactions. It depends therefore on the heats of adsorption of the reacting gases as well as on the octivation energy of the homogeneous reaction.

It is therefore necessary to qualify the simple explanation offered in the preceding section of the similarity of the platinum and quartz igniting points. If the initial reaction is a heterogeneous one on the sphere surface, the equivalence of platinum and quartz is probably fortuitous, the net results of different

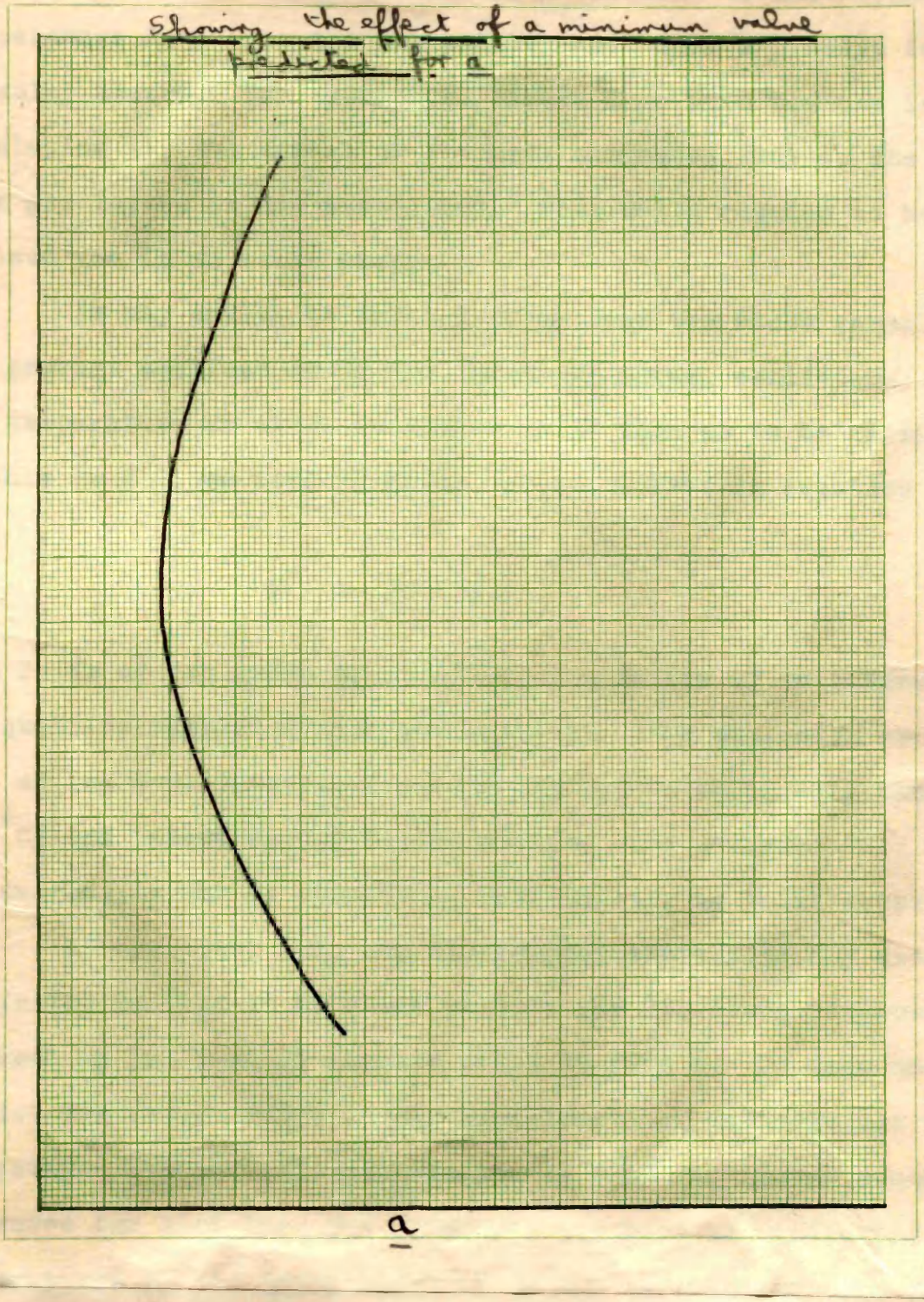
adsorption relationships being the same. Enough is not yet known about the adsorption of pentane, hydrogen, and air on platinum and quartz to supply a test. In our hydrogen experiments it is clear from the agreement between the predicted activation energy and that recent value given by Semenova, that either the initial shell reaction was homogeneous or the heats of adsorption of hydrogen and oxygen on platinum are such as not to alter the apparent activation energy appreciably. The former alternative is probably the case for pentane.

Further, criticism of the expression in equation (8) may be made from the standpoint of what happens when a is made very small. On general grounds it is clear that a can diminish to zero provided the temperature be made infinite. Our expression fails to satisfy this requirement. If we differentiate it we get

$$\frac{da}{dT} = a\left\{\frac{1}{T-T_0} - \frac{A}{RT^2}\right\} \qquad \ldots\ldots\ldots (8)$$

so that a has turning values when the bracket term is zero. If a has a minimum value we get a curve similar to that in fig. 9 which means that the sphere can ignite only at points within the obtuse angle of the curve, and that above the upper curve, it cannot ignite. This anomaly arises from our assumption that the rate of heat loss from the initial shell is proportional to the temperature excess of the sphere, so that at a sufficiently high temperature it again loses heat more rapidly than the combustion produces, i.e. it is <u>too hot</u> to ignite. This does not mean that

Fig. 9.



ignition does not occur; it must when the loss of heat brings the temperature down into the allowed region. Such a process is actually absurd. The expression breaks down here because in developing it, the effect of the heat conducted away on the recipient gas layers is not considered. This would require to be allowed for in an exact theory.

It may easily be shewn however that the above anomaly need not prevent application of the theory to normal conditions, for the temperature at which it arises is so high as to be meaningless. If this is T', we find by equating the bracket in equation (7) to zero

$$T' = \left(\frac{A}{R} - T_o\right)$$

Thus T' is of the order of $10,000^{o}C$, a quantity of no interest in the question connected with gas ignition, (the explosion temperature of the most powerful blasting explosives being only about $5000^{o}C$) and indeed having little meaning as a temperature. Hence, the expression may be considered satisfactory up to at least $5000^{o}C$.

At the other end, the theoretical expression may also be criticised in that it does not predict the "ignition temperatures" observed by the various authors cited in Part I. It does however predict the values found in our experiments on particle ignition correctly. The probable explanation is that the theory makes no allowance for time-lag, and gives its accuracy in predicting temperatures of the order observed in our experiments from the fact that ignition by the sphere must be practically instantaneous,

since it is in motion. If time lag were allowed for, igniting temperatures might conceivably be reduced, since into the theory would come the amount of heat produced after a given time as well as initial rate of heat production. The theoretical expression may therefore be considered as very good above about 700°C where time-lags become small.

Section 6.

Conclusions on the theory advanced.

The characteristics of ignition of a gaseous mixture at atmospheric pressure by a moving hot sphere are adequately represented by the theory of a certain thermal limiting condition developed in this thesis. The conditions prevailing are not suitable for the incidence of purely chain explosions. The theory explains the existence of a minimum igniting temperature dependent on particle size and leads to an expression which can be used, provided certain constants in it are known, to calculate the minimum temperature at which a sphere of a given size will ignite a given gas mixture. The constants involved refer to the chemical kinetics of the reaction, and some of them, particularly the energy of activation may readily be determined from a set of results such as obtained in our experiments - if the theory is valid. This point is of considerable importance, since it offers a very convenient and simple method of determining activation energies of gas reactions in the explosive region. Here the activation energy cannot be determined by usual methods, since these involve measurement of a finite reaction velocity. It is hoped that the method will prove of use to workers in this field. Similar considerations hold if the reactions occurring are heterogeneous.

Further, once the constants are determined from a set of experimental results, it becomes possible to calculate the igniting temperatures of spheres so small as to be inconvenient for experiment. This is of great importance in connection with the ignition

of gas mixtures by hot solid products from detonating explosives, such as can occur in coal mining (cf. Part I.). Knowing the temperature of explosion one can calculate the maximum safe size of solid particle allowable in the products, or conversely if it is known that a certain maximum size of particle is produced on disintegration, a safe limit can be assigned to the explosion temperature. For example, we may calculate the minimum size of particle, from an explosive whose explosion temperature is 3000°C, which will ignite a 7% methane-air mixture. In our experiments a sphere of radius 0.325 cms. ignited at 1200°C. Applying the derived formula to these figures and using the value of 61,400 cals/gm.mol. given by Hinshelwood and Fort[18] for the activation energy of the methane oxidation we find the constant Log $\frac{\beta Q}{2P}$ = 12.71. Using this value, with the above value of A, we find a minimum required radius of 7.7×10^{-6} cms. at 3000°C. Solid particles from the explosive would be capable of igniting a 7% methane air atmosphere if they exceeded this size.

Sufficient knowledge of the size of particles created by friction is not available to allow calculation of igniting temperatures for such sparks. Given such data, the calculations could be made readily on the above hypotheses.

The theory is approximate, and does not hold rigidly for a tending to zero and for a tending to infinity, since it does not show an infinite temperature in the first case, nor is the expression asymptotic to the ignition temperature in the second. In spite of this, it is shown to be satisfactory at least in the temperature

range 700°-5000°C. This is just the range which is of interest in the problems enumerated in the introduction.

Values of kinetic constants derived by the application of the theory to the experiments on pentane and hydrogen, described in Part II, are in general agreement with known values from other work. Such agreement, together with its satisfactory qualitative interpretation of the results observed in our experiments, constitute strong support for the theory.

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B. APPENDIX.

ON THE APPLICATION OF CERTAIN HEAT CONDUCTION SOLUTIONS FOR A UNIFORM MEDIUM TO THE TEMPERATURE DISTRIBUTION IN THE GAS SURROUNDING A METAL SPHERE.

INTRODUCTION.

In connexion with the experiments on the ignition of gaseous mixtures by heated spheres, the writer found it desirable to obtain an expression for the distribution of temperature in the gas surrounding a metal sphere of known initial temperature. The expression was required to allow numerical calculation of the temperature and temperature gradients at a point in the gas. A search through the literature of heat conduction problems failed to produce such an expression. So far as the writer is aware, no solution capable of arithmetical treatment has been given to the above general problem. Robertson[1] has given a solution using the wave-train method developed by Green[2], but it is not convenient for numerical evaluation. The direct methods of Fourier analysis are inapplicable, because the co-existence of the different media destroys the conditions which allow determination of coefficients. R. E. Langer[3] has explained a method of overcoming this difficulty in the case of a certain cylindrical problem. This may be capable of development for the case of a sphere immersed in a different medium, but it is again doubtful if it would lend itself to arithmetical treatment. The internal temperatures in a sphere with known surface conditions are discussed by J. H. Awbery[4], but an external medium is not considered. Carslaw[5], by conventional analysis, and Bromwich[6], by the Heaviside "operational method," treat of the temperatures in a sphere with a surrounding thin shell of different material. Their solutions admit of numerical calculation, as do those of

Awbery, but the condition that the outer medium is a thin shell renders them inapplicable to the present problem.

Thus, since no exact solution was found for the general problem, we sought for a good approximation that might be taken to serve for our special circumstances. The argument proceeded as follows. There are several known solutions of the Fourier equation for temperature distribution in a uniform conducting medium. It seemed reasonable therefore to consider what conditions prevailing in a uniform medium would approach most closely to those produced in the gas by the presence of the sphere. It is then possible that some of the known solutions might fulfil such conditions. Then, by identifying the gas with the uniform medium and considering only temperatures outside a radius equal to the radius of the metal sphere, it was thought that a serviceable approximation to the actual temperature distribution would be found. Such solutions have been investigated and may be used, in the manner indicated by the present paper, to give arithmetical values required in connexion with experimental work on ignition. Apart, however, from this application, the form of the combination of solutions for a uniform medium may be of theoretical interest in showing how the source and sink method due to Kelvin may be applied to satisfy arbitrary additional conditions. It must be remarked, however, that the solutions discussed are considered only with regard to certain very limited intervals of time, such as those which are alone concerned in explosion work.

The Condition assumed in the Uniform Medium.

The first step is to enquire what conditions may be assumed to exist in the metal sphere and gas problem. They are:-

(a) That the gas in contact with the surface of the metal has the temperature of the surface.

(b) That this temperature at the sphere surface may be assumed to be constant at its initial value for a short but finite time.

We are neglecting entirely convection and radiation, so that these assumptions are justified by the following considerations:-

(1) The thermal capacity of the gas per unit volume is very much less than that of the metal, and its conductivity is also much smaller. The gas in contact with the sphere must thus be raised almost immediately to the surface temperature.

(2) Again, because of the large difference in capacity, the heat lost by the sphere will have comparatively little effect on its temperature, although it causes considerable rise in the adjacent gas.

We are, in fact, treating the thermal capacity of the sphere as infinite in comparison with that of an equal volume of gas, and are regarding the surface temperature of the sphere as practically constant during a short interval of time. Thus, since our object is to find the temperature state in the space

outside the sphere, we may change to a uniform medium problem simply by regarding the sphere as an apparatus for maintaining a spherical surface at constant temperature for a short but finite time. We now enquire whether the above conditions can be satisfied by superposing the known effects of certain sources in a uniform medium.

The Maintenance of Constant Temperature at a Spherical Surface in a Uniform Medium.

The Fourier equation for a spherically symmetrical distribution of temperature in a uniform medium is

$$\frac{\partial^2\theta}{\partial r^2} + \frac{2}{r}\frac{\partial\theta}{\partial r} = \frac{1}{k}\frac{\partial\theta}{\partial t} \qquad \ldots\ldots\ldots (1)$$

where k is the thermometric conductivity of the medium, i.e., its thermal conductivity K divided by its specific heat per unit volume c. The following solutions of equation (1) are known for the different types of source indicated:-

(1) Instantaneous point source, generating amount of heat q:

$$\theta = \frac{q\, e^{-\frac{r^2}{4kt}}}{8c(\pi k t)^{\frac{3}{2}}} \qquad \ldots\ldots\ldots (2)$$

(Fourier, 'Theorie de la Chaleur,' § 385.)

(2) Continued point source, supplying q units of heat per second:

$$\theta = \frac{q}{2kc\pi^{3/2}r}\int_{\frac{r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx \qquad \ldots\ldots (3)$$

(Taylor-Jones, Morgan, and Wheeler, Phil. Mag. xliii. p.364 (Feb. 1922.))

(3) Instantaneous spherical surface source, supplying Q units of heat distributed uniformly over the whole surface, radius b:

$$\theta = Q\,\frac{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}}{8cbr\pi^{3/2}(kt)^{1/2}} \qquad \ldots\ldots (4)$$

(Lord Kelvin, Enc. Brit. 9th ed. Art. "Heat," Appendix)
The expression there should be divided by π.

(4) Instantaneous spherical volume source radius b, total heat supply Q:

$$\theta = \frac{3Q}{4cb^3\pi^{3/2}}\left\{\int_0^{\frac{r+b}{2\sqrt{kt}}} e^{-x^2}dx - \int_0^{\frac{r-b}{2\sqrt{kt}}} e^{-x^2}dx\right\}$$

$$-\frac{3Q}{4cb^3\pi^{3/2}}\,\frac{(kt)^{1/2}}{r}\left\{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}\right\} \qquad \ldots\ldots (5)$$

(Taylor-Jones, Morgan, and Wheeler, loc. cit. p. 367.)

To those we may add:

(5) A continued spherical surface source supplying heat Q per second. The distribution due to this source can be derived by integrating equation (4), thus:

$$\theta = Q \int_0^t \frac{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}}{8cbr\pi^{\frac{3}{2}}(kt)^{\frac{1}{2}}}\,dt \qquad \ldots\ldots\ldots (6)$$

Where $r < b$, the substitution $x = \frac{b-r}{2\sqrt{kt}}$ leads to the expression

$$\theta = \frac{Q}{4\pi^{\frac{3}{2}}bc}\left[\left(\frac{t}{k}\right)^{\frac{1}{2}} \frac{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}}{r}\right]$$

$$- \frac{Q}{4\pi^{\frac{3}{2}}bc}\left[\frac{b-r}{kr}\int_{\frac{b-r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx - \frac{b+r}{kr}\int_{\frac{b+r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx\right] \qquad \ldots\ldots (7)$$

When $r > b$ the required substitution is $x = \frac{r-b}{2\sqrt{kt}}$, and gives

$$\theta = \frac{Q}{4\pi^{\frac{3}{2}}bc}\left[\left(\frac{t}{k}\right)^{\frac{1}{2}} \frac{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}}{r}\right]$$

$$- \frac{Q}{4\pi^{\frac{3}{2}}bc}\left[\frac{r-b}{kr}\int_{\frac{r-b}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx - \frac{r+b}{kr}\int_{\frac{r+b}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx\right]$$

$$\ldots\ldots\ldots (8)$$

Now let a be the radius of the surface whose temperature is desired to maintain constant. We may begin by determining the effect of source (4) in the uniform medium. Let T_0 be written for $\frac{3Q}{4\pi a^3 c}$, the initial temperature of the source. If the resulting distribution is denoted by θ_1, we have

$$\theta_1 = \frac{T_0}{\sqrt{\pi}}\left\{\int_0^{\frac{r+b}{2\sqrt{kt}}} e^{-x^2}dx - \int_0^{\frac{r-b}{2\sqrt{kt}}} e^{-x^2}dx\right\} - \frac{T_0}{\sqrt{\pi}}\frac{(kt)^{\frac{1}{2}}}{r}\left\{e^{-\frac{(r-b)^2}{4kt}} - e^{-\frac{(r+b)^2}{4kt}}\right\} \qquad (9)$$

Then at the surface r = a,

$$\left(\frac{\partial\theta_1}{\partial t}\right)_{r=a} = \frac{T_0}{\sqrt{\pi}}\left\{\frac{a-b}{4\sqrt{k}\,t^{\frac{3}{2}}}e^{-\frac{(a-b)^2}{4kt}} - \frac{a+b}{4\sqrt{k}\,t^{\frac{3}{2}}}e^{-\frac{(a+b)^2}{4kt}}\right\} - \frac{T_0}{\sqrt{\pi}}\frac{k^{\frac{1}{2}}}{2at^{\frac{1}{2}}}\left\{e^{-\frac{(a-b)^2}{4kt}} - e^{-\frac{(a+b)^2}{4kt}}\right\} + \frac{T_0}{\sqrt{\pi}}\frac{(kt)^{\frac{1}{2}}}{a}\left\{e^{-\frac{(a+b)^2}{4kt}}\frac{(a+b)^2}{4kt^2} - e^{-\frac{(a-b)^2}{4kt}}\frac{(a-b)^2}{4kt^2}\right\} \qquad (10)$$

Let b = a. i.e., let the instantaneous volume source have the required surface as its boundary. Then

$$\left(\frac{\partial\theta_1}{\partial t}\right)_{r=a} = \frac{T_0 a}{2\sqrt{\pi k}}\cdot\frac{e^{-\frac{a^2}{kt}}}{t^{\frac{3}{2}}} - \frac{T_0}{2\sqrt{\pi}}\frac{k^{\frac{1}{2}}}{at^{\frac{1}{2}}}\left\{1 - e^{-\frac{a^2}{kt}}\right\} \qquad (11)$$

Since for small values of t, $e^{-\frac{a^2}{kt}}$ is very small, the negative term in (11) is much larger than the positive. θ_1 thus gives a rapid fall in temperature at r = a. It is clear that no choice of constants can make $\left(\frac{\partial \theta_1}{\partial t}\right)_{r=a}$ zero at all times. We can, however, superimpose another source upon that already present so as to obtain a resulting time derivative whose modulus is much less than that of $\left(\frac{\partial \theta_1}{\partial t}\right)_{r=a}$. For we see from equation (4) that the distribution due to an instantaneous surface source has $t^{-\frac{1}{2}}$ as a factor, as does the negative term in equation (11). This expression is, however, the time derivative of the distribution due to a continuous spherical surface source, as given in equations (7) and (8). Thus we may denote the distribution due to the continuous surface source by θ_2 and add it to θ_1. Since

$$\left(\frac{\partial \theta_2}{\partial t}\right)_{r=a} = \frac{Q\left\{e^{-\frac{(a-b)^2}{4kt}} - e^{-\frac{(a+b)^2}{4kt}}\right\}}{8ca^2b\pi^{3/2}(kt)^{\frac{1}{2}}} \qquad (12)$$

if we let the radius b of this source also equal a, then

$$\left(\frac{\partial \theta_2}{\partial t}\right)_{r=a} = \frac{Q}{8ca^2\pi^{3/2}(kt)^{\frac{1}{2}}}\left\{1 - e^{-\frac{a^2}{kt}}\right\} \qquad (13)$$

Adding this to $\frac{\partial \theta_1}{\partial t}$ and putting $\theta = \theta_1 + \theta_2$, we get

$$\left(\frac{\partial \theta}{\partial t}\right)_{r=a} = \frac{T_0 a}{2\sqrt{\pi k}} \cdot \frac{e^{-\frac{a^2}{kt}}}{t^{3/2}} + \frac{1 - e^{-\frac{a^2}{kt}}}{t^{\frac{1}{2}}}\left\{\frac{Q}{8ca^2\pi^{3/2}k^{\frac{1}{2}}} - \frac{T_0 k^{\frac{1}{2}}}{2\sqrt{\pi}a}\right\} \qquad (14)$$

Clearly $Q = 4\pi a c k T_0$ makes the second term vanish for all values of t. This gives the value of the rate of heat supply which must be supposed in the superimposed surface source. We are left with

$$\left(\frac{\partial\theta}{\partial t}\right)_{r=a} = \frac{T_0\, a}{2\sqrt{\pi k}} \cdot \frac{e^{-\frac{a^2}{kt}}}{t^{\frac{3}{2}}} \qquad \text{(15)}$$

This positive residual quantity cannot in itself be considered negligible, but it will be shown by calculating arithmetical values of the expression for θ given by the superimposition of the two above solutions that its effect during small intervals of time is negligible for at least a satisfactory length of time.

The expression for θ admits of convenient simplification, for, putting $Q = 4\pi a c k T_0$ in the superimposed part, we get, for $r<a$,

$$\theta = \frac{T_0}{\sqrt{\pi}}\left\{\int_0^{\frac{a+r}{2\sqrt{kt}}} e^{-x^2}dx + \int_0^{\frac{a-r}{2\sqrt{kt}}} e^{-x^2}dx\right\} - \frac{T_0}{\sqrt{\pi}}\,\frac{(kt)^{\frac{1}{2}}}{r}\left\{e^{-\frac{(r-a)^2}{4kt}} - e^{-\frac{(r+a)^2}{4kt}}\right\}$$

$$+ \frac{kT_0}{\sqrt{\pi}}\left[\left(\frac{t}{k}\right)^{\frac{1}{2}} \frac{e^{-\frac{(r-a)^2}{4kt}} - e^{-\frac{(r+a)^2}{4kt}}}{r} - \frac{a-r}{kr}\int_{\frac{a-r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx + \frac{a+r}{kr}\int_{\frac{a+r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx\right] \qquad \text{(16)}$$

$$\therefore\ \theta = \frac{T_0}{\sqrt{\pi}}\left\{\int_0^{\frac{a+r}{2\sqrt{kt}}} e^{-x^2}dx + \int_0^{\frac{a-r}{2\sqrt{kt}}} e^{-x^2}dx\right\}$$

$$- \frac{T_0}{\sqrt{\pi}}\left(\frac{a-r}{r}\right)\int_{\frac{a-r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx$$

$$+ \frac{T_0}{\sqrt{\pi}}\left(\frac{a+r}{r}\right)\int_{\frac{a+r}{2\sqrt{kt}}}^{\infty} e^{-x^2}dx \qquad \text{(17)}$$

Some of the definite integrals combine to give

$$\int_0^\infty e^{-x^2}\,dx \quad \text{which is } \frac{\sqrt{\pi}}{2}$$

and θ becomes

$$= T_0 - \frac{T_0}{\sqrt{\pi}}\,\frac{a}{r}\int_{\frac{a-r}{2\sqrt{kt}}}^{\infty} e^{-x^2}\,dx + \frac{T_0}{\sqrt{\pi}}\,\frac{a}{r}\int_{\frac{a+r}{2\sqrt{kt}}}^{\infty} e^{-x^2}\,dx \quad , \quad r<a \qquad \ldots\ldots (18)$$

Similar simplification of the corresponding expression for $r > a$ gives, since the signs of some of the definite integrals are changed,

$$\theta = \frac{T_0}{\sqrt{\pi}}\,\frac{a}{r}\int_{\frac{r-a}{2\sqrt{kt}}}^{\infty} e^{-x^2}\,dx + \frac{T_0}{\sqrt{\pi}}\,\frac{a}{r}\int_{\frac{r+a}{2\sqrt{kt}}}^{\infty} e^{-x^2}\,dx \quad , \quad r>a \qquad (19)$$

This is zero when $t = 0$, as is required. Moreover, the expressions (18) and (19) agree when $r = a$, and we have, when $t \neq 0$,

$$\theta_{r=a} = \frac{T_0}{2} + \frac{T_0}{\sqrt{\pi}}\int_{\frac{a}{\sqrt{kt}}}^{\infty} e^{-x^2}\,dx \qquad (20)$$

Now because of the instantaneous volume source, the initial temperature of the surface $r = a$ is T_0. But a characteristic of the distribution due to that source is that the surface temperature, as soon as t is not zero, drops to $T_0/2$ (vide Taylor-Jones, Morgan and Wheeler, loc. cit. p. 367). The same happens in our case, but then the growth of temperature due to the coincident continued spherical surface source compensates for any further

fall. The temperature at r = a is then appreciably constant at $T_0/_2$, until the term $\frac{T_0}{\sqrt{\pi}} \int_{\frac{a}{\sqrt{kt}}}^{\infty} e^{-x^2} dx$ becomes significant. This is clearly seen from equation (20). The smaller the radius a, the sooner will the rise in temperature be appreciable.

Tables I and II show the distribution given by θ at various times for values of a respectively 0.25 cm. and 0.1 cm. They show that this combination of sources, which we shall call Solution I, does serve to keep the surface r = a at constant temperature for an appreciable time after t = 0. They also indicate the time at which the temperature at the surface begins to rise perceptibly. The temperatures are shown as fractions of T_0, and are calculated for air, taking k = 0.5.

The plotting of these values in figs. 1 and 2 shows clearly how the distribution curves rotate round the point r = a, $\theta = T_0/_2$ as t increases, for small times.

The Application to the Metal and Gas Problem.

This has been made directly by taking $T_0/_2$ as the original temperature of the metal sphere and a as its radius. The values given above, for r > a, can then be used as approximations to the temperature distribution in the gas, so long as the time in question is one for which the rise in temperature at r = a is

TABLE I.

Solution I. a = 0.25 cm.

t, seconds.	Temperature / T_o at r cm.							
	0	0.22	0.25	0.26	0.30	0.35	0.45	0.60
0.0001	1.0000	0.9984	0.5000	0.1527	0	0	0	0
0.001	0.9999	0.8053	0.5000	0.3613	0.0475	0.0006	0	0
0.01	0.9123	0.5657	0.5000	0.4423	0.257	0.1135	0.0125	0
0.02	0.7044	0.5278	0.5002	0.4536	0.3016	0.1713	0.0437	0.0027

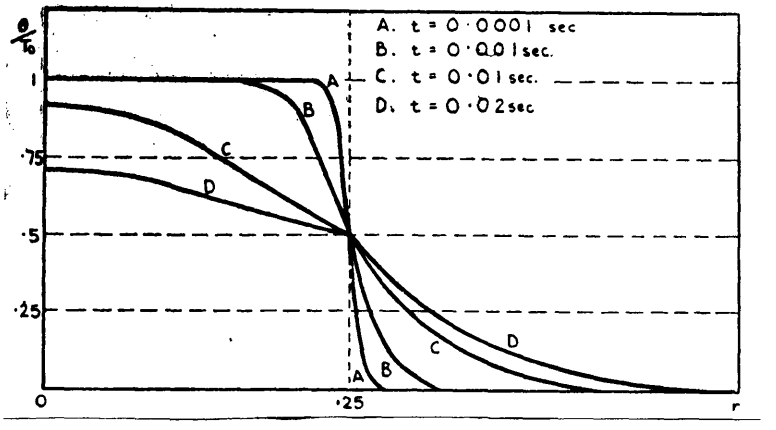
TABLE II.

Solution I. a = 0.1 cm.

t, seconds.	Temperature / T_o at r cm.							
	0	0.07	0.1	0.11	0.13	0.20	0.25	0.35
0.0001	1	0.9980	0.5000	0.1444	0.0011	0	0	0
0.001	0.9653	0.7552	0.5000	0.3416	0.1318	0.0004	0	0
0.02	0.5160	0.5194	0.5227	0.4345	0.3022	0.0801	0.0268	0.0017

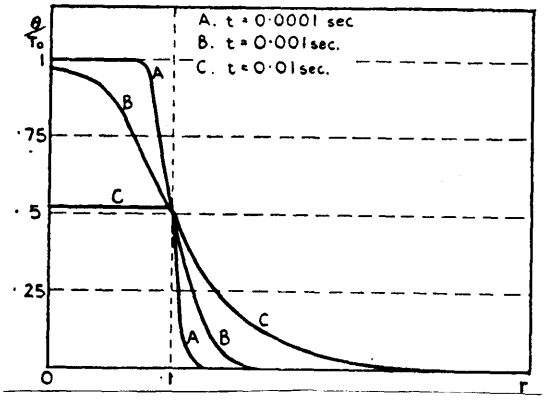
negligible. Tables I and II thus give us an idea of the limit of time up to which Solution I may be applied to the metal sphere and gas problem. This time may be called the Limit of Application of Solution I. For a = 0.25 cm. it is somewhat greater than 0.02 second, and for a = 0.1 cm. it is about 0.01 second. We are, of course, here concerned only with temperatures in the gas outside the radius r = a, and the portions of the curves in figs. 1a and 2a for $r > 0.25$ cm. and > 0.1 cm. respectively are thus assumed to give the required values.

Fig. 1a



Solution I. a = 0.25 cm.

Fig. 2a.



Solution I. a = 0.1 cm.

It may be pointed out that, in making this application, the instantaneous temperature T_o of the surface of the instantaneous volume source in the uniform medium is entirely ignored. This is justifiable, considering the suddenness of the drop to $T_o/2$.

An Alternative Solution.

We have seen that Solution I causes a rise in temperature at r = a when the initial period of constancy is past. This is a distinct difference from the conditions prevailing in the sphere and gas problem, where the temperature must begin to fall. It is possible, however, to add another of the spherical solutions given on pp. 78–80 to Solution I so as to obtain a distribution which indicates falling temperature at r = a, after a preliminary period of approximate constancy. (The instantaneous volume source alone would, of course, provide such a fall of temperature, but this would be much too rapid for the conditions of our problem, since it would make no allowance for the capacity of the sphere relative to that of the gas.)

This second solution, which we shall call Solution II, may be obtained as follows:- Let the distribution given by Solution I be denoted by ϕ . Then

$$\left(\frac{\partial \phi}{\partial t}\right)_{r=a} = \frac{T_o\, a}{2\sqrt{\pi k}} \; \frac{e^{-\frac{a^2}{kt}}}{t^{3/2}} \qquad \ldots\ldots (21)$$

Examining the list of known solutions, we find that equation (2), which represents the distribution due to an instantaneous point source, consists of a term in $t^{-\frac{3}{2}}$ i.e., the derivative of a continuous point source solution consists of a term in $t^{-\frac{3}{2}}$, which is the power of t in equation (21). So let us imagine that we have, in addition to the sources of Solution I, a continuous point sink at the centre, which absorbs heat q per second. If the resulting distribution is now θ, we have

$$\left(\frac{\partial\theta}{\partial t}\right)_{r=a} = \frac{T_0\, a}{2\sqrt{\pi k}} \frac{e^{-\frac{a^2}{kt}}}{t^{\frac{3}{2}}} - q \frac{e^{-\frac{a^2}{4kt}}}{8c(\pi kt)^{\frac{3}{2}}} \quad \ldots (22)$$

Defining q as $4\pi a c k T_0$ this becomes

$$\left(\frac{\partial\theta}{\partial t}\right)_{r=a} = \frac{T_0\, a}{2\sqrt{\pi k}} \cdot \frac{e^{-\frac{a^2}{kt}} - e^{-\frac{a^2}{4kt}}}{t^{\frac{3}{2}}} \quad \ldots (23)$$

Now $e^{-\frac{a^2}{4kt}} > e^{-\frac{a^2}{kt}}$, so that $\left(\frac{\partial\theta}{\partial t}\right)_{r=a}$ is negative, ~~at r = a.~~

The expression for the temperature distribution due to all three sources superimposed now becomes:

(a) $r > a$,

$$\theta = \frac{T_0\, a}{\sqrt{\pi}\, r} \int_{\frac{r-a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx + \frac{T_0}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{r+a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx$$

$$- \frac{2T_0}{\sqrt{\pi}} \cdot \frac{a}{r} \int_{\frac{r}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx \quad - - - \quad (24)$$

(b) $r < a$,

$$\theta = T_0 - \frac{T_0}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{a-r}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx + \frac{T_0}{\sqrt{\pi}} \frac{a}{r} \int_{\frac{a+r}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx$$

$$- \frac{2T_0}{\sqrt{\pi}} \cdot \frac{a}{r} \int_{\frac{r}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx \qquad (25)$$

The temperature at r = a according to (24) and (25) is

$$\theta_{r=a} = \frac{T_0}{2} + \frac{T_0}{\sqrt{\pi}} \int_{\frac{a}{\sqrt{kt}}}^{\infty} e^{-x^2} dx - \frac{2T_0}{\sqrt{\pi}} \int_{\frac{a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx \qquad (26)$$

We see that this is approximately constant at $T_0/2$, until the term $- \frac{2T_0}{\sqrt{\pi}} \int_{\frac{a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx$ becomes significant. It then begins to fall. This occurs much sooner than the rise in Solution I, as is shown by the numerical values given (also for a = 0.25 cm. and a = 0.1 cm.) in Tables III. and IV. The corresponding curves for Solution II are given in figs. 3a and 4a.

Now if we are to confine the use of Solutions I and II in the metal sphere and gas problem only to values of t for which the surface temperature may be assumed constant, Solution II will cease to apply sooner than the first, since $2 \int_{\frac{a}{2\sqrt{kt}}}^{\infty} e^{-x^2} dx$ becomes significant before $\int_{\frac{a}{\sqrt{kt}}}^{\infty} e^{-x^2} dx$. We see from equations (19) and (25) that the two solutions give identical distributions for r > a, up to the time when the second begins to

fall at r = a. After that, II has a smaller gradient than I. For r < a they do not coincide, because the presence of the sink requires $-\infty$ for the temperature at the centre.

TABLE III.

Solution II. a = 0.25 cm.

t, seconds.	Temperature / T_o at r cm.							
	0	0.22	0.25	0.26	0.30	0.35	0.45	0.60
0.0001	$-\infty$	0.9984	0.5000	0.1527	0	0	0	0
0.001	$-\infty$	1.0000	0.5000	0.3613	0.0475	0.0006	0	0
0.01	$-\infty$	0.5340	0.4875	0.4334	0.2548	0.1135	0.0125	0
0.02	$-\infty$	0.3917	0.4232	0.3911	0.2734	0.1618	0.0873	0.0027

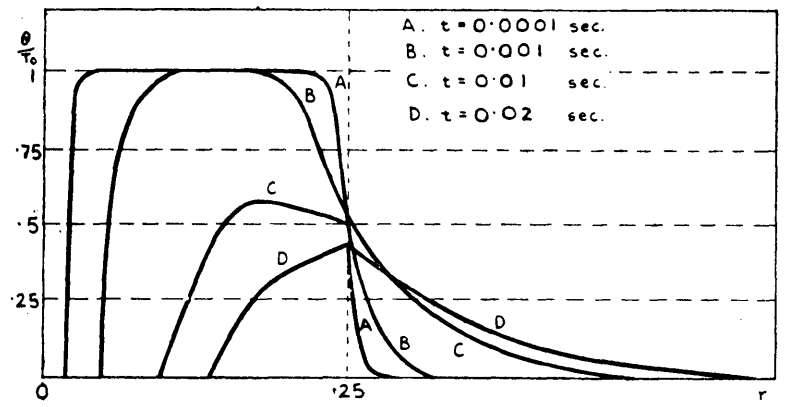
TABLE IV.

Solution II. a = 0.1 cm.

t, seconds.	Temperature / T_o at r cm.							
	0	0.07	0.10	0.11	0.13	0.20	0.25	0.35
0.0001	$-\infty$	0.9980	0.5000	0.1444	0.0011	0	0	0
0.001	$-\infty$	0.7011	0.4984	0.3412	0.1318	0.0004	0	0
0.01	$-\infty$	0.2969	0.2150	0.1878	0.1530	0.0576	0.0218	0.0017

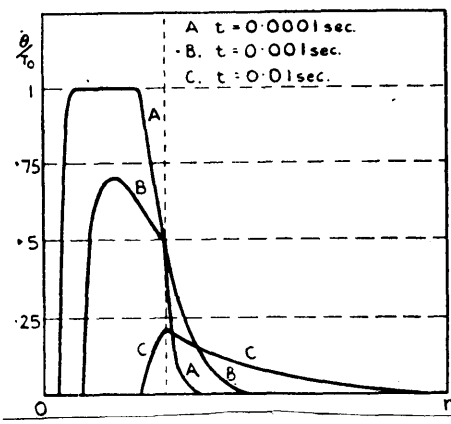
Since the distributions are at first equal for $r > a$, the question as to which of the two solutions is more suitable in the application is simply the question of how long we are entitled to assume constancy of temperature at the surface of the metal sphere. It depends, therefore, on the capacity of the metal sphere relative to that of the gas. The larger this is, the longer we can assume constancy to continue, so that for a very large capacity we may use Solution I up to its limit of constancy. With a sphere of smaller capacity constancy can only be assumed to last for a shorter time, so that it may be un-

Fig. 3.a



Solution II. a = 0.25 cm.

Fig. 4.a



Solution II. a = 0.1 cm.

suitable to use the solutions for times after the beginning of the fall of temperature at r = a in Solution II.

It is possible that a still closer approximation to the conditions of the sphere and gas problem, applicable to still later times, could be arrived at by superposing the effects of a fourth or a fifth hypothetical source in a uniform medium, but it is thought that for the purposes of the experimental work in connection with which these calculations were undertaken, Solutions I and II give a sufficiently close approximation, provided they are not used beyond their time limitations.

It is tempting to suppose that Solution II will continue to hold as an approximation to the distribution in the gas even after it shows appreciable fall in the surface temperature, since this actually occurs with the metal sphere. The same, however, might be said for an instantaneous volume source alone, except for the difference in degree. Solution II only represents an improvement upon the instantaneous volume solution in so far as, its fall of temperature at r = a being more gradual, it allows for the capacity of the sphere. This allowance may be inadequate if it is used beyond the point we have discussed. Hence it is advisable meantime to confine the application of these solutions in the problem of the temperature distribution in the gas round a metal sphere rigidly to the supposition of constant temperature maintained at the surface of the sphere.

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